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Characterization of Ash from Coal-Fired Power Plants

Tennessee Valley Authority, Chattanooga Power Research Staff

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CHARACTERIZATION OF ASH FROM COAL-FIRED POWER PLANTS

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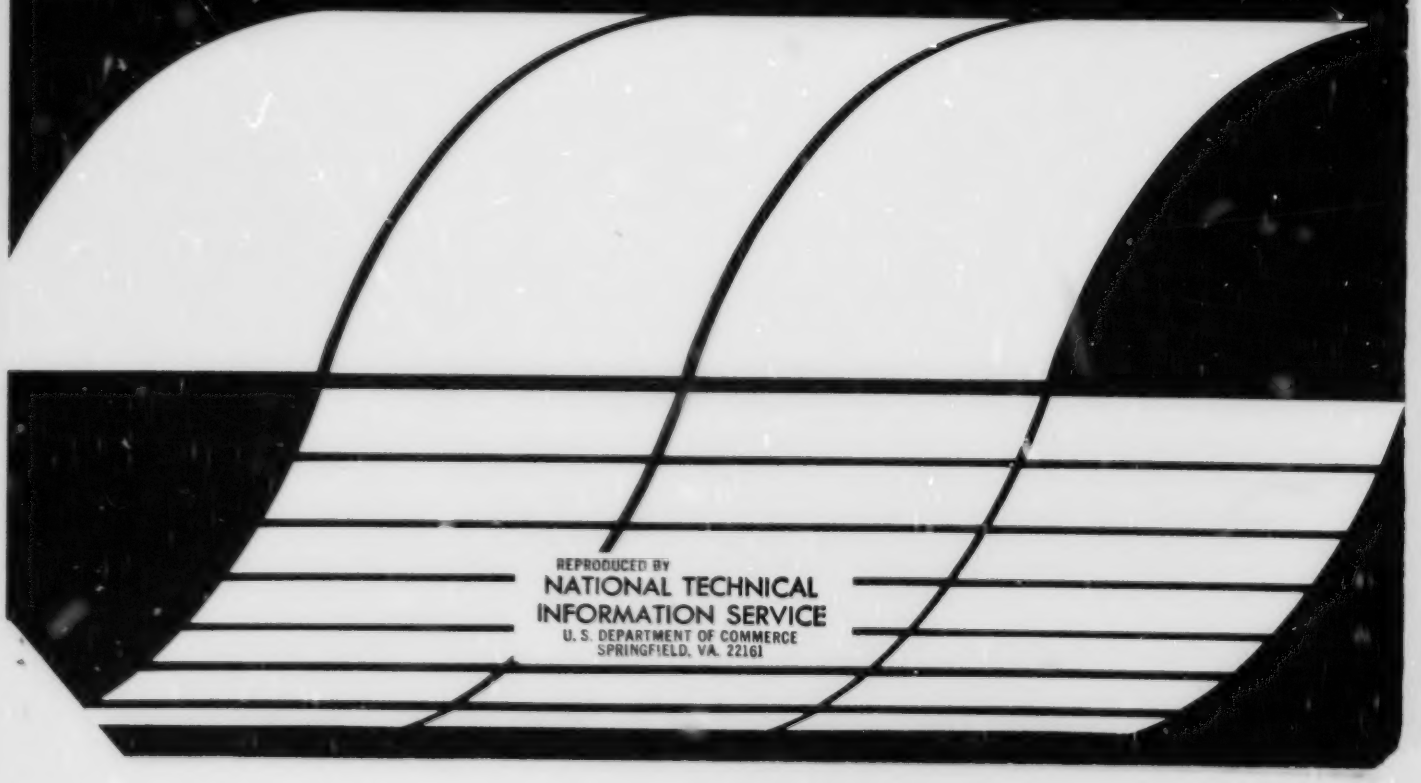

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ABSTRACT

This report presents a summary of existing data on the chemical and physical characteristics of ashes produced by the burning of coal in steam-electric generating plants. Several recent coal or ash characterization studies are summarized; emphasis is placed on the elemental chemical composition, particularly trace inorganic constituents. General agreement among the studies is found regarding partitioning of trace elements among the bottom ash, fly ash, and flue gas. Coal and ash analysis methods are examined to aid in evaluation and comparison of results from studies which do not all use identical analytical methods. The need for a standard set of analytical procedures for coal and ash is evident. The physical and chemical characteristics of sulfur dioxide scrubbing sludges are also summarized because these materials are becoming a significant portion of total power plant residues.

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CONVERSION TABLE

A list of conversion factors for British units used in this report is as follows:

British	Metric
1 inch	2.54 centimeters
1 foot	0.3048 meter
1 mile	1.609 kilometers
1 pound	0.454 kilogram
1 ton (short)	0.9072 metric tons
1 gallon	3.785 liters
1 part per million	1 milligram per liter (equivalent)
1 part per billion	.001 milligram per liter (equivalent)
1 British thermal unit per pound	2.235 Joules per gram

SECTION 1

INTRODUCTION

The passage of the Federal Air Quality Act in 1970 necessitated examination of the impact of steam-electric power plants on the atmospheric environment. Subsequent passage of the Federal Water Pollution Control Act of 1972 (PL 92-500) and the resulting requirement that National Pollutant Discharge Elimination System permits be obtained at all steam plants have made it important to determine the overall impact a steam-electric power plant will have on the aquatic environment as well. Thus, it is essential that air emissions and water discharges from such plants be characterized.

The combustion of coal produces a residue composed of inorganic mineral constituents and incompletely burned organic matter. During the combustion process potentially hazardous pollutants are released, some of which are introduced into the environment. As the quantity of coal utilized increases, the amounts of these potential pollutants produced grows proportionately. Some trace elements found in coal and ash are toxic to certain plants and animals at relatively low concentrations. Therefore, characterization of combustion products is increasingly important for assessment of the concentrations, the amounts, and the forms in which pollutants may be released to the environment.

Additionally, characterization of coal ash will later be helpful in determining new and more extensive uses or improved disposal methods for this combustion product. At present a relatively small proportion (about 14 to 16 percent) of ash is utilized; the remainder presents a significant disposal problem.

The purpose of this report is to present a summary of existing data on the chemical and physical characteristics of coal ashes produced by the burning of coal in steam-electric generating plants.

This report addresses the characteristics of the coals from which the ashes are derived as well as those of the ashes themselves. Several recent studies concerned with the characteristics of coal, ash, or ash effluents are examined, with emphasis on the elemental chemical composition of the coals and their ashes, particularly the trace inorganic constituents. Methods for the chemical analysis of ash and coal matrices are examined to aid the evaluation and comparison of results from studies which did not all use the same analytical methods. The physical and chemical characteristics of sulfur dioxide scrubbing sludges are also summarized because these materials are becoming a significant portion of total power plant residues.

SECTION 2

CONCLUSIONS

The use of coal, the most widely distributed fuel in the United States, is increasing at a rapid rate. In 1974 the utilities industry utilized 390 million tons; it is estimated that by 1984 this industry will use 800 million tons per year. The coal used in the future may contain greater amounts of ash, as coal seams with larger ash proportions are increasingly explored and utilized. The combination of these two factors, greater coal usage and larger proportions of ash, will result in increasing total amounts of ash residues.

Many elements are enriched in coal, compared to their abundance in the earth's crust, and enriched in ash, compared to their concentrations in the coal.

Analytical studies of coal and its combustion residues generally agree that elements are partitioned into three main groups with respect to their distribution in the residues, as follows.

1. Group I - Elements which are approximately equally distributed in the bottom ash and the flyash.
2. Group II - Elements which are preferentially concentrated in the flyash as compared to the bottom ash.
3. Group III - Elements which are primarily emitted to the atmosphere as gaseous species.

The theory for this partitioning effect involves the volatilization of some elements or their compounds in the furnace. Subsequently, some of these vaporous phase elements recondense, either partially or completely; others are discharged through the stack as gases. Elements with volatilization temperatures higher than that reached in the boiler remain about evenly distributed in the two ash fractions (Group I). Others are volatilized and are not cooled sufficiently to condense (Group III). Elements which do condense generally form fine particles or are deposited onto the surface of small particles (Group II).

The finer particulates in flyash are a particular source of environmental concern, because three factors combine to make them an especial risk over that presented by larger particles.

1. Fine particulates have proportionally higher concentrations of many potentially hazardous trace elements.
2. They pass through collection devices and are emitted to the atmosphere in greater proportions.
3. They enter more easily into the human respiratory system and are retained for longer periods.

SECTION 3

RECOMMENDATIONS

In order to better assess the impact of power plant emissions and effluents and to improve ash disposal and utilization practice, a more complete understanding is needed of potentially hazardous pollutants generated by power plants, including the quantities, and the distributions among various power plant emissions/effluents. Several studies have been made to determine the pollutant quantities and distributions but more work in these areas would better define potential environmental effects.

A problem encountered in previous studies has been the difficulty of obtaining representative samples from the various effluent streams, especially of the gases and fine particulates in stack emissions. The two-phase flows in bottom ash and flyash sluicing waters are another example of this problem. It is suggested that research be continued toward the development of improved sampling instrumentation and the recommendation of uniform, standardized techniques.

Results from analytical studies on power plant residues are not always comparable, because of differences in analytical methods used to determine particular elements and in sample preparation and handling. These sources of error are in addition to the normal interlaboratory data dispersion which occurs when multiple institutions prepare and analyze the same sample using identical techniques. It is recommended that standard analytical practices be developed for general usage for trace elements in the coal and ash matrices.

As stricter air pollution laws proliferate, new combustion methods, coal preparation, or residue treatments will be required to comply with these laws. Most of the concepts proposed to meet these laws (such as flue gas desulfurization, coal liquefaction and gasification, increased usage of certain types of coals, and new power plant designs) will result in increased quantities and/or altered characteristics of power plant residues. Research is needed into the characteristics of these products, as well as into the distribution of possibly hazardous trace elements and other pollutants contained in the residues.

In order to identify the extent of the impact which the ash stored in ash ponds may have on the environment, it is suggested that studies be conducted on the leachability of trace elements from the pond into the surrounding soils and groundwater.

SECTION 4

SUMMARY AND DISCUSSION

Coal, the most widely distributed fuel in the United States, is found in 38 states. The nation's total coal resources have been estimated at about 4 trillion tons, nearly half of which is thought to be recoverable reserves. The coals from the wide range of locations across the country include fuels varying significantly with respect to heat content, ash content, and chemical properties.

Coalification resulted from the subjection of peat (plant debris) swamps to high temperature and pressure for millions of years. The degree of coalification depends on the degree of heat and pressure. The ash content of the coal thus formed was influenced by the extent to which overburden material was dispersed throughout the coal seam. Trace elements carried by rainwater, streams, or surface waters were deposited in the peat swamps and thus incorporated into the coal.

The major elemental components of coal are carbon, hydrogen, oxygen, nitrogen, and sulfur. Organic constituents were derived from the decay of plant material, while inorganic constituents were derived from the earth's crustal formations which surrounded the peat swamp. Many trace elements have been shown by the Bureau of Mines to be concentrated in coals with respect to their concentrations in the earth's crust.

Coal combustion results in a residue consisting of the inorganic mineral constituents in the coal and the organic matter which is not fully burned. The inorganic mineral constituents, whose residue is ash, make up from 3 to 30 percent of the coal. During combustion, this ash is distributed into two parts, bottom ash (collected from the bottom of the boiler unit) and flyash (most of which is collected by air pollution control equipment through which the stack gases pass). A third residue, vapors, is that part of the coal which is volatilized in the furnace. Most of the vapors are emitted to the atmosphere in the stack gas.

The distribution of ash between the bottom and flyash fractions is a function of the following:

1. Boiler type (firing method). The type of firing is perhaps the most important factor in determining ash distribution. Stoker fired units emit the smallest proportion of flyash. In cyclone

units 80-85 percent of the ash is melted and collected as slag. Pulverized coal units produce 60 to 85 percent flyash and the remainder bottom ash.

2. Coal type (ash fusion temperature). Ashes with lower fusion temperatures tend to melt within the furnace and, therefore, to be collected as bottom ash.
3. Wet or dry bottom furnace. Wet bottom boilers are designed to produce and process a much larger proportion of bottom ash than are dry bottom boilers.

Flyash makes up from 10 percent to 85 percent of the coal ash residue and occurs as spherical particles, usually ranging in diameter from 0.5 to 100 microns. Color varies from light tan to black, depending on the carbon content. An interesting portion of flyash is made up of very lightweight particles called cenospheres, which comprise up to 20 percent by volume of the flyash. These cenospheres are spheres of silicate glass filled with nitrogen and carbon dioxide which range from 20μ to 200μ in diameter. They are "floaters" which create a suspended solids problem in pond disposal of ash. The chemical composition of cenospheres is very similar to that of flyash.

The bottom ash, composed primarily of coarser, heavier particles than the flyash, ranges from gray to black in color and is generally angular with a porous surface. If it is collected as a slag, these slag particles usually are black, angular, and have a glass-like appearance.

Petrographic analysis has shown that glass is the primary component of ash, constituting 50-90 percent of the total weight. Finer particles generally contain a higher proportion of the glass constituent than the coarser ones. Other components of the ash include magnetite, hematite, carbon, mullite, and quartz.

The chemical characteristics of ash depend largely on the geologic and geographic factors related to the coal deposit. The major constituents of ash--primarily silicon, aluminum, iron, and calcium--make up 95 to 99 percent of the total composition. Minor constituents, such as magnesium, titanium, sodium, potassium, sulfur, and phosphorus, comprise 0.5 percent to 3.5 percent. Ash also contains trace concentrations of from 20 to 50 elements, including, for example: antimony, arsenic, barium, beryllium, boron, copper, fluorine, lead, manganese, mercury, molybdenum, nickel, selenium, tellurium, thallium, tin, titanium, uranium, vanadium, and zinc.

With the steady growth in coal utilization in this country, the quantities of potentially hazardous pollutants entering the environment as the result of coal combustion increase also. Table 1 displays the amounts of elements mobilized into the atmosphere each year as a result of weathering processes and the combustion of fossil fuels. Many of these elements are mobilized into the atmosphere in excess of 1000 tons per year (1×10^9 grams≈1100 tons). The full impact of these pollutants is unknown.

TABLE 1. AMOUNTS OF ELEMENTS MOBILIZED INTO THE ATMOSPHERE AS A RESULT OF WEATHERING PROCESSES AND THE COMBUSTION OF FOSSIL FUELS[a] (1)

Element	Fossil fuel concentration (ppm)		Fossil fuel mobilization ($\times 10^9$ g/year)			Weathering mobilization ($\times 10^9$ g/year)	
	Coal	Oil	Coal	Oil	Total	River flow	Sediments
Beryllium	3	0.0004	0.41	0.00006	0.41	-	5.6
Boron	75	0.002	10.5	0.0003	10.5	360	-
Sodium	2,000	2	280	0.33	280	230,000	57,000
Aluminum	10,000	0.5	1400	0.08	1400	14,000	140,000
Chlorine	1,000		140				280,000
Calcium	10,000	5	1400	0.82	1400	540,000	70,000
Titanium	500	0.1	70	0.02	70	180	9,000
Vanadium	25	50	3.5	8.2	12	32	280
Chromium	10	0.3	1.4	0.05	1.5	36	200
Manganese	50	0.1	7	0.02	7	250	2,000
Iron	10,000	2.5	1400	0.41	1400	24,000	100,000
Cobalt	5	0.2	0.7	0.03	0.7	7.2	8
Nickel	15	10	2.1	1.6	3.7	11	160
Copper	15	0.14	2.1	0.023	2.1	250	80
Zinc	50	0.25	7	0.04	7	720	80
Arsenic	5	0.01	0.7	0.002	0.7	72	
Selenium	3	0.17	0.42	0.03	0.45	7.2	
Molybdenum	5	10	0.7	1.6	2.3	36	28
Cadmium		0.01		0.002			0.5
Tin	2	0.01	0.28	0.002	0.28		11
Barium	500	0.1	70	0.02	70	360	500
Mercury	0.012		0.0017	1.6	1.6	2.5	1.0
Lead	25	0.3	3.5	0.05	3.6	110	21

[a]This table is condensed from that of Bertine and Goldberg.[1]

Several studies have been made recently to determine the concentrations of these trace elements in the coal combustion residues. These studies were conducted on different sizes and types of systems with respect to megawatt output, collector configuration, boiler type, and operating conditions. Even the purposes of the studies differed. Yet, they were in fairly close agreement as to their findings on the distribution of elements among different fractions of the combustion residues.

Most of these studies agreed that elements were distributed into the fractions of coal combustion residue (bottom ash, flyash, and vapors) according to definite patterns. The elements appeared to be divided into three main classes, as follows.

1. Elements which are approximately equally concentrated in the bottom ash and flyash.
2. Elements which are enriched in the flyash relative to their concentrations in the bottom ash.
3. Elements which are primarily discharged to the environment as gases.

Results from an analytical study conducted at the Tennessee Valley Authority's Allen Steam Plant[2] partitioned elements into the above categories as shown in Table 2. The elements Cr, Cs, Na, Ni, U, and V were not placed into one of these three groups but were judged to exhibit behavior intermediate between the first two groups. Lee[3] also found Sb, Pb, Se, and Zn preferentially concentrated in submicron-sized particles (Group II) but added Cr to this group as well as Ni, which he found concentrated in particles in the 5-10 micron range. Natusch[4] agreed that As, Cd, Pb, Sb, Se, Zn, Cr, and Ni fell into this group of elements showing pronounced concentration in smaller flyash particles. He placed two other elements, Tl and S, into this group also. Gordon (Chalk Point Station)[5] again placed As, Sb, Pb, and Se in this group and labeled iodine as a member of the group. Jorden (Valmont Station)[6] named As, Sb, Cu, Pb, Mo, and Zn to the group of elements increasingly enriched with downstream location. Results from a study of three Northern Great Plains plants[7-10] showed that As, Sb, Se, V, Pb, Mo, Ni, B, Zn, Cd, Cr, Cu, Co, U, Ag, S, Hg, Cl, and F were enriched in the flyash plus flue gas samples, with S, Hg, Cl appearing to be emitted from the plant as gaseous species. Thus, in examining just one category, i.e., elements preferentially concentrated in the flyash, the conclusions of several studies are generally consistent. This agreement of results is notable, considering the differences in the furnace types, coal types, and sampling and analytical procedures.

Elements named by one or more studies as primarily emitted to the atmosphere in the vaporous phase include Cl, F, Br, Hg, S, and Se. Most sulfur is emitted as SO_x and the halogens as hydrogen halides, all of which are scrubbed in an alkaline SO_x scrubber (CaO, $CaCO_3$, or $NaSO_3$).

Obtaining representative samples for coal and ash characterization is often difficult because of variations in coals and complications in stack sampling, particularly for fine particulate. Comparisons in characterization also are impeded by differences in the analytical methods chosen.

TABLE 2. PARTITION OF ELEMENTS BY THEIR TENDENCIES FOR DISTRIBUTION IN COAL COMBUSTION RESIDUES (2)

Group I						
Elements Concentrated Approximately Equally in Bottom Ash and Flyash						
Al	Ce	Fe	La	Rb	Sm	Th
Ba	Co	Hf	Mg	Sc	Sr	Ti
Ca	Eu	K	Mn	Si	Ta	

Group II			
Elements Preferentially Concentrated in the Flyash			
	As	Ga	Sb
	Cd	Mo	S
	Cu	Pb	Zn

Group III	
Elements Tending to be Discharged to Atmosphere as Vapors	
Hg	Cl
	Br

The methods used for chemical analysis of coal and ash can be separated generally into two categories. One category includes methods by which multiple element determinations can be easily made on a single sample. These methods often do not require sample preparation; analysis may be performed on the sample directly. Examples of these methods are instrumental neutron activation analysis, instrumental photon activation analysis, X-ray fluorescence, spark source mass spectrometry, and optical emission spectroscopy. Methods in the second category usually require considerable sample preparation for the coal and flyash matrices in order to avoid or reduce interferences. They may require, too, larger quantities of sample if more than a few elements are to be determined. These methods include atomic absorption spectroscopy, potentiometry, voltammetry, and absorption spectrophotometry.

Results from studies which used different methods of analysis may not be strictly comparable because of differences in performance capabilities among these methods. In comparing determinations on the same samples by different laboratories each using several methods, reported concentrations for trace elements were often found to vary by more than an order of magnitude. However, a study testing nuclear methods,[11] such as instrumental neutron activation, photon activation, and natural radioactivity, found their accuracy and interlaboratory dispersion generally superior to those of other methods. Standard samples and standard methods of analysis are needed for comparable determinations of trace element concentrations in power plant inlet and effluent streams. A committee of the American Society of Testing and Materials is presently working to develop standard techniques for coal and ash analyses.

SECTION 5

COAL CHARACTERIZATION

GENERAL

The United States' most widely distributed fuel, coal, is found in 38 states.[13] The coals from this wide range of locations include fuels with extensive variations in heat content, ash content, and chemical properties. It has been estimated that the coal resources of the United States include 3,968 billion tons with approximately 2,000 billion tons reclaimable using present technology.[13] The cumulative total production of coal is 42.3 billion tons with approximately 21 billion tons produced since 1933. The utilities industry in 1974 utilized 390 million tons and by 1984 the industry is expected to use 800 million tons a year.[14]

The ASTM classification (ranking) of coals which is commonly used in the United States is based primarily on the percent volatile matter and calorific values. Figure 1 presents the ranking of coals according to these factors. Geological and mining research has shown that coal rank can be correlated with geological structure and geographical location of the coal deposits. The geographical locations of U.S. coals (by rank) are shown in Figure 2.

ORIGIN

The coal fields were formed from ancient peat swamps which were subjected to intense heat and pressure for millions of years. The temperature and pressure were accomplished by the deposition of rocks and soils from the area around the swamps as the swamps subsided. The subsidences were formed at depths of up to 7,000 meters where a temperature of 200°C and a pressure of 1,500 kg/cm^2 can occur.[15] The degree of coalification depends on the temperature and pressure to which the swamp was subjected. Catastrophic earth movements which formed the mountains probably formed many of the coal fields.

The ash content and the trace element concentration, however, are influenced by the manner in which the subsidence occurs, i.e., whether the subsidence is a single occurrence or a multioccurrence, in which there are alternate layers of swamps and overburden. The coal produced from a multioccurrence subsidence will tend to have a greater ash content, especially when the coal is used "as mined," unless extreme care is exercised during mining to prevent the inclusion of the overburden material at the top and the foreign

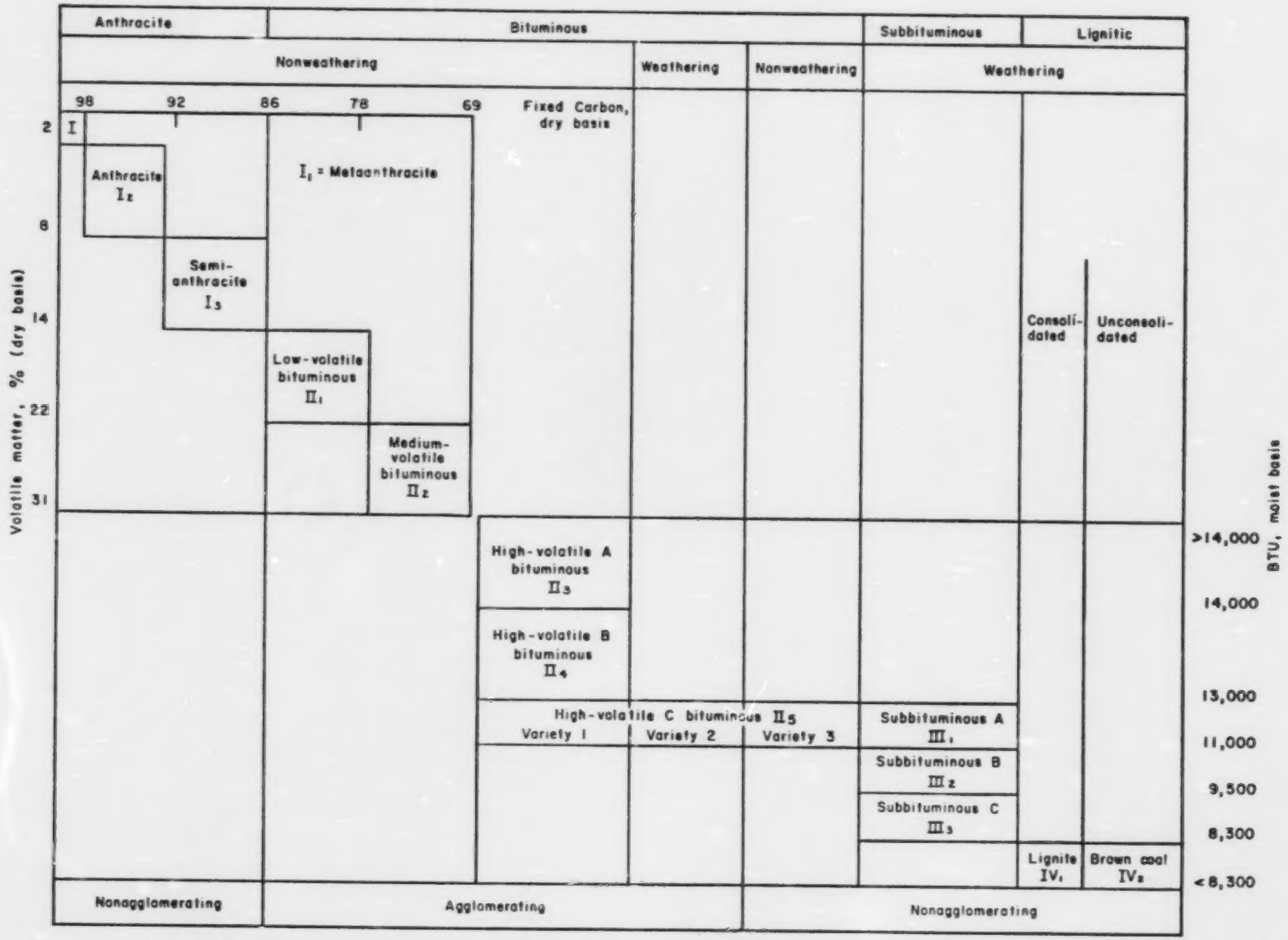

Figure 1. ASTM classification of coals by rank. Courtesy American Society for Testing & Materials. (16)

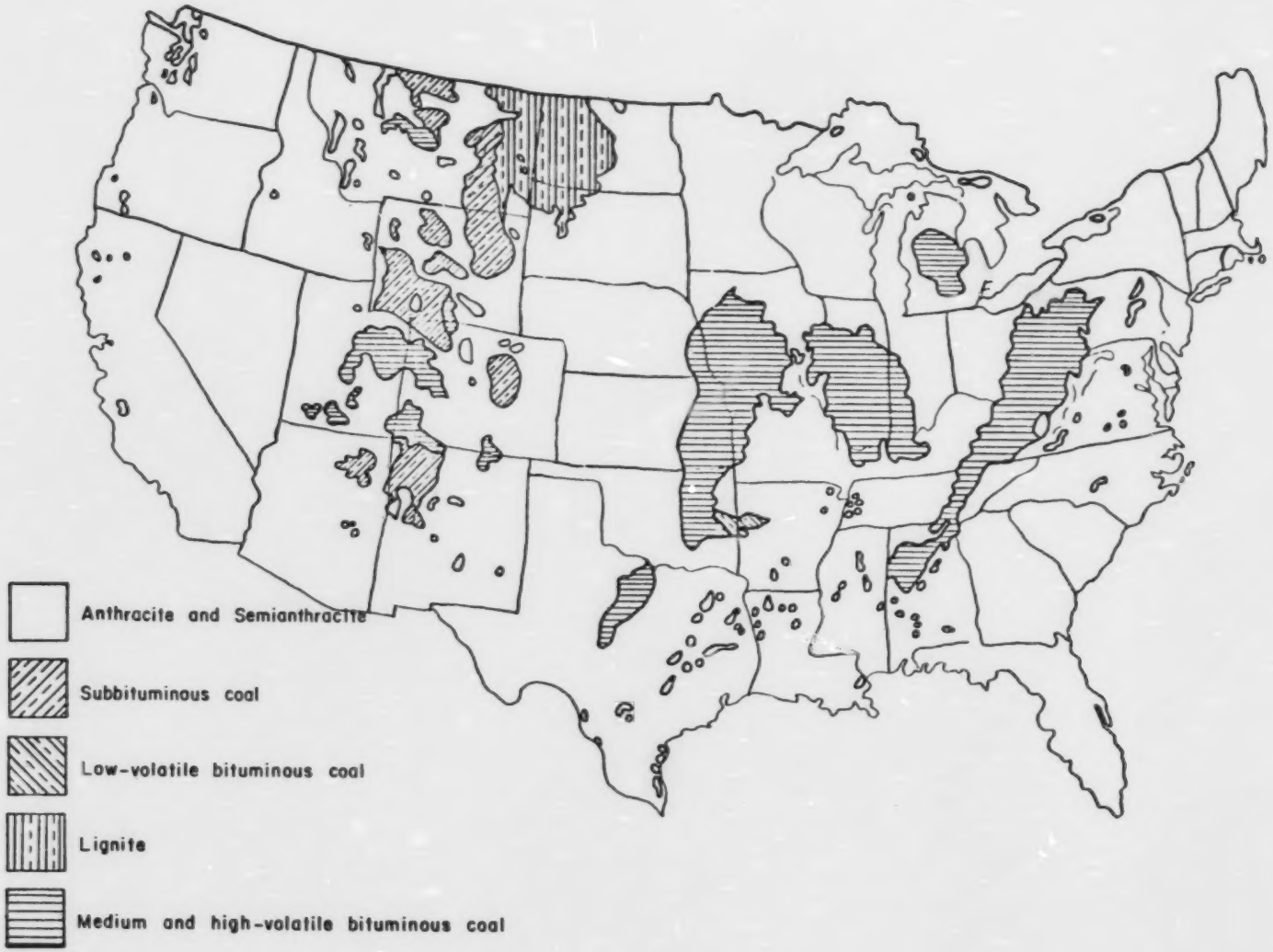

Figure 2. Coal fields of the conterminous United States. (13)

matter at the bottom of the seam. Also, in many cases, the overburden material during subsidence will form thin layers (1/8- to 1/2-in.) throughout the coal seam which will be reclaimed with the coal, again causing an increased ash content.[15]

There are three means whereby trace elements may be incorporated into the coal. These methods are the following.

1. Syngenetic - Elements are deposited from surface waters by living plants or in dead organic matter in swamps prior to coalification.
2. Diagenetic - Elements are introduced into the coal during coalification by waters bringing the elements from areas marginal to the coal deposits or from the consolidating enclosing sediments.
3. Epigenetic - Elements are introduced into the coal after coalification and after consolidation of the enclosing sediments by ground water deriving elements from unconformably overlying rocks and soils.[4]

The components of peat have a large potential for trapping many elements; however, the actual concentrations of trace elements in coal are highly variable and are, in fact, quite low in some parts of a swamp. For example, suppose the peat swamp was located in a basin surrounded by hills. The rocks in the hills were eroded over time by natural processes. During this process, trace elements were released along with chemically altered mineral grains and washed by rain and streams down into the basin. Heavy inorganic metals tended to be trapped in the margins of the swamp. The center of the coal seam formed from that swamp then tended to contain lower concentrations of trace elements.[15]

CHARACTERIZATION

The major elemental components of coal are carbon, hydrogen, oxygen, nitrogen, and sulfur. Empirical formulas have been found to range from $C_{75}H_{140}O_{56}N_2S$ for a low grade peat to $C_{240}H_{90}O_4NS$ for a high grade anthracite coal.[5] These formulas exclude the ash content of the coals, which ranges from 3 percent to 30 percent. The variations in the coal formulas and in the ash content can be attributed to the conditions under which the coalification of peat swamps occurred.

Organic constituents of coals are derived from the decay of plant material, which consists of vitrinite (the wood parts), sporinite (the waxy coating of spores and pollen), fusinite (charcoal from forest fires), and micrinite (origin unknown). Inorganic constituents are derived from the earth's crustal formations which surround the peat swamps.[15]

Inorganic chemical constituents of coal can be separated into three major categories with respect to their relative concentrations in the coal. The grouping includes major constituents (greater than 1 percent), minor constituents (generally, 0.1 percent to 1 percent), and trace constituents (less than 0.1 percent). The concentration ranges for the major and minor

elements in coal ash are given in Table 3 for the four main types of coals, while the concentration ranges for the trace elements are given in Table 4. The elements listed in Table 4 are of primary interest in this report because they may be potential health or environmental hazards after they are discharged into the environment. Furthermore, the Bureau of Mines has shown that many of these trace elements are concentrated in coals with respect to their abundance in the earth's crust. The enrichment in coal ash of a few of these elements can be seen in Table 5 and that part of the enrichment which may come from the decay of peat is shown as a percentage of coal ash in Table 6. For example, ash from oak humus is enriched over ash from fresh oak leaves by a factor of 2 for NiO and by a factor of 14 for GeO_2.

When characterizing the effluent from a power plant, the percentage of the chemical elements which are volatilized or released to the environment must be determined experimentally in all streams leaving the plant; even then, the results must be used with caution. The wide ranges in concentration of the elements from a given coal seam or basin (see Table 7) are an indication of the sizeable variability which may be expected in experimental results from a power plant. The need for caution in interpreting results is further illustrated by considering the data from a report by Billings et al.[17] on a mercury balance for a fossil fuel plant. The study which they conducted was a 3-day sampling program of the incoming coal (from one seam) and all discharge streams. They reported that the mercury concentration in the coal for the three days was 0.7 ppm, 0.1 ppm, and 0.2 ppm, respectively, and that the quantities of coal used during the corresponding time period were 8,552 tons; 8,428 tons; and 8,548 tons. If the average concentration of mercury (.33 ppm) were used to characterize the incoming coal, the respective daily mercury input would have been 5.64 lb, 5.56 lb, and 5.64 lb. Instead, on an actual day-to-day basis, the input was 11.97 lbs, 1.69 lbs, and 3.42 lbs. Further, the results of the flue gas vapor tests indicated that on the first day of the test 9.3 lbs of mercury was discharged into the atmosphere, while 2.2 lbs and 0.98 lbs were discharged on the following two days. If the difference between the mercury in the coal and that in the flue gas vapor is taken as the quantity remaining in the ash, it would appear that 2.7 lbs, -0.5 lbs, and 2.4 lbs, respectively, of mercury was contained in the ash. The analysis of the various ash collection points, however, showed that on all three days there was 0.6 lbs total mercury in the ash. Thus, it is important that especial care be exercised in the sampling and analysis processes in this type of study.

TABLE 3. VARIATIONS IN COAL ASH COMPOSITION WITH RANK (18)

Rank	% SiO_2	% Al_2O_3	% Fe_2O_3	% TiO_2	% CaO	% MgO	% Na_2O	% K_2O	% SO_3	% Ash
Anthracite	48-68	25-44	2-10	1.0- 2	0.2- 4	0.2- 1	-	-	0.1- 1	4-19
Bituminous	7-68	4-39	2-44	0.5- 4	0.7-36	0.1- 4	0.2- 3	0.2- 4	0.1-32	3-32
Subbituminous	17-58	4-35	3-19	0.6- 2	2.2-52	0.5- 8	-	-	3.0-16	3-16
Lignite	6-40	4-26	1-34	0.0-0.8	12.4-52	2.8-14	0.2-28	0.1-1.3	8.3-32	4-19

TABLE 4. CONCENTRATIONS OF TRACE ELEMENTS IN COAL (5)

Element	Concn in whole coal (ppm)	Source[a]	Analytical[b] method	% Ash
Antimony	0.6-1.5	A	NAA	6.15-18.27
	0.1-2.0	A	SSMS	-
	<1	IE	INAA	10.9-11.2
	0.2-8.9	IE	NAA	3.28-16.04
	1.2	IW	NAA	25.85
	0.9	N	NAA	11.29-15.83
	<0.2-0.6	SW	NAA	6.56-13.65
	<0.05-1.76	SW	AS	3.85-29.60
Arsenic	5.1-35.0	A	NAA	6.15-18.27
	3.0-10.0	A	SSMS	-
	3.0-59.0	A	-	-
	3.8-18.0	IE	INAA	11.2
	1.7-93	IE	NAA	3.28-16.04
	9.3	IW	NAA	25.85
	1.2-2.5	N	NAA	11.29-15.83
	0.5-1.3	SW	NAA	6.58-13.65
	<1.0-4.0	SW	AS	3.85-29.60
	5.44	Av U.S.	-	-
Barium	20-400	A	SSMS	-
	79-91	IE	INAA	10.9-11.2
	40-1600	SW	SSMS	-
Beryllium	2.0-3.1	A	-	-
	0.6-2.6	A	OES	6.15-18.27
	0.4-3.0	A	SSMS	-
	<2	IE	-	6.80-17.26
	2.5	IE	-	-
	<5	IE	SSMS	10.9-11.2
	0.5-4.0	IE	OES	3.28-16.04
	1.2	IW	OES	25.85
	0.64-2.3	IW	-	-
	1.0-1.1	N	OES	11.29-15.83
	0.12-3.9	N	-	-
	0.4	SW	SSMS	-
	0.2-1.4	SW	OES	6.56-13.65
Boron	22-55	A	-	-
	5-83	A	OES	6.15-18.27
	1-120	A	SSMS	-
	96	IE	-	-
	100-200	IE	SSMS	10.9-11.2
	12-216	IE	OES	3.28-16.04
	66	IW	OES	25.85
	84-92	N	OES	11.29-15.83
	20-216	SW	SSMS	-
	17-138	SW	OES	6.56-13.65

(continued)

TABLE 4 (continued). CONCENTRATIONS OF TRACE ELEMENTS IN COAL (5)

Element	Concn in whole coal (ppm)	Source	Analytical method	% Ash
Cadmium	<0.6	A	AAS	6.15-18.27
	0.04-0.7	A	SSMS	-
	30-<300	IE	-	6.80-17.26
	0.44-0.50	IE	SSMS-ID	10.9-11.2
	<0.1-65	IE	AAS	3.28-16.04
	11.0	IW	AAS	25.85
	<0.4	N	AAS	11.29-15.83
	0-0.6	SW	-	-
	<0.6	SW	AAS	6.56-13.65
	<0.01-3.0	SW	SSMS	-
Chlorine (wt %)	0.0006-0.10	A	SSMS	-
	0.15			
	0.04-0.37	A	XRF	6.15-18.27
	0.13-0.28	IE	INAA	6.80-17.26
	0.01-0.54	IE	XRF	3.28-16.04
	0.06	IW	XRF	25.85
	0.01-0.02	N	XRF	11.29-15.83
	0.001-0.003	SW	SSMS	-
	0.01-0.03	SW	XRF	6.56-13.68
Chromium	11-15	A	-	-
	8.49-10.9	A	OES	-
	10-23	A	OES	6.15-18.27
	26-400	A	SSMS	-
	≤20	IE	-	12.6-13.4
	20	IE	-	-
	21-23	IE	INAA	10.9-11.2
	4-54	IE	OES	3.28-16.04
	22	IW	OES	25.85
	5-7	N	OES	11.29-15.83
	2-8	SW	SSMS	-
	5-8	SW	OES	6.56-13.65
Cobalt	4.1-6.7	A	-	-
	2-12	A	SSMS	-
	90			
	5-33	A	OES	6.15-18.27
	3.8	IE	-	-
	3.3-5.0	IE	INAA	10.9-11.2
	2-34	IE	OES	3.28-16.04
	43	IW	OES	25.85
	2	N	OES	11.29-15.83
	1-8	SW	SSMS	-
	1-7	SW	OES	6.56-13.65

(continued)

TABLE 4 (continued). CONCENTRATIONS OF TRACE ELEMENTS IN COAL (5)

Element	Concn in whole coal (ppm)	Source	Analytical method	% Ash
Copper	14-17	A	-	-
	3-180	A	SSMS	-
	11-28	A	AAS/OES	6.15-18.27
	5-20	IE	-	6.8-10.9
	11	IE	-	-
	50-100	IE	SSMS-ID	10.9-11.2
	5-33	IE	AAS/OES	3.28-16.04
	61	IW	AAS/OES	25.85
	15-18	N	AAS/OES	11.29-15.83
	15	N	-	-
	1-15	SW	-	-
	10-22	SW	AAS/OES	6.56-13.65
	60-180	SW	SSMS	-
	9.6	SW	XRF	6
Fluorine	50-120	A	-	-
	1-19	A	SSMS	-
	110			
	50-125	A	ISE	6.15-18.27
	50-100	IE	-	-
	30-143	IE	ISE	3.28-16.04
	65-120	IW	-	-
	91	IW	ISE	25.85
	60-70	N	-	-
	42-52	N	ISE	11.29-15.83
	8	SW	SSMS	-
	39-105	SW	ISE	6.56-13.68
	<50.0-220.0	SW	ISE	3.85-29.60
Lead	4-14	A	-	-
	4-18	A	AAS/OES	6.15-18.27
	2-36	A	SSMS	-
	8-14	IE	-	-
	7.4	IE	SSMS-ID	10.9-11.2
	4-218	IE	AAS/OES	3.28-16.04
	102	IW	AAS/OES	25.85
	4	IW	-	-
	7	N	AAS/OES	11.29-15.83
	7	N	-	-
	1-2	SW	SSMS	-
	4-7	SW	AAS/OES	6.56-13.65
Manganese	5-48	A	SSMS	-
	9-55	A	NAA	6.15-18.27
	25-95	IE	-	6.8-17.26
	51-54	IE	INAA	10.9-11.2
	6-181	IE	NAA	3.28-16.04
	108	IW	NAA	25.85
	88-101	N	NAA	11.29-15.83

(continued)

TABLE 4 (continued). CONCENTRATIONS OF TRACE ELEMENTS IN COAL (5)

Element	Concn in whole coal (ppm)	Source	Analytical method	% Ash
Manganese (Cont.)	6-22	SW	NAA	6.56-13.68
	10-240	SW	SSMS	-
	5-200	-	OES	-
Mercury	0.12-0.21	A	-	-
	<0.3-0.5	A	SSMS	-
	0.08-0.46	A	NAA	6.15-18.27
	0.16-1.91	IE	-	6.80-17.26
	0.13	IE	-	-
	0.170-0.063	IE	FAAS	10.9-11.2
	0.04-1.60	IE	NAA	3.28-16.04
	0.19	IW	-	-
	0.18	IW	NAA	25.85
	0.07	N	-	-
	0.07-0.09	N	NAA	11.29-15.83
	0.11-0.74	SE	FAAS	10.63-18.58
	0.02-0.06	SW	NAA	6.56-13.68
	<0.3	SW	SSMS	-
	0.02-1.20	SW	FAAS	3.85-29.60
	0.07	SW	FAAS	6
	0.05-0.38	-	NAA/AAS	-
Molybdenum	1.5-5.8	A	-	-
	1-5	A	SSMS	-
	10			
	1-11	A	OES	6.15-18.27
	4.3	IE	-	-
	10-20	IE	SSMS	10.9-11.2
	<1-29	IE	OES	3.28-16.04
	2.6-4.3	IW	-	-
	14	IW	OES	25.85
	8-30	N	OES	11.29-15.83
	<1-2	SW	OES	6.56-13.68
	1-4	SW	SSMS	-
	0.99	SW	XRF/WC	-
Nickel	9.7-20.0	A	-	-
	3-60	A	SSMS	-
	11-22	A	XRF/OES/AAS	6.15-18.27
	<20-90	IE	-	6.8-10.9
	15	IE	-	-
	8-68	IE	XRF/OES/AAS	3.28-16.04
	80	IW	XRF/OES/AAS	25.85
	11-24	IW	-	-
	4-6	N	XRF/OES/AAS	11.29-15.83
	4	SW	SSMS	-
	3-8	SW	XRF/OES/AAS	6.56-13.68
	10-30	SW	OES	-

(continued)

TABLE 4 (continued). CONCENTRATIONS OF TRACE ELEMENTS IN COAL (5)

Element	Concn in whole coal (ppm)	Source	Analytical method	% Ash
Selenium	0.04-0.3	A	SSMS	-
	1.3-6.6	A	NAA	6.15-18.27
	2.6-3.4	IE	INAA	10.9-11.2
	0.4-7.7	IE	NAA	3.28-16.04
	2.9	IW	NAA	25.85
	0.8	N	NAA	11.29-15.83
	0.5-3.9	SW	-	-
	1.2-2.3	SW	NAA	6.58-13.68
	0.40-3.90	SW	XRF	3.85-29.60
	1.9	SW	XRF	6
Tellurium	<0.1-0.4	A	SSMS	-
	1-3	IE	SSMS	10.9-11.2
	0.2	SW	SSMS	-
	<0.02-0.10	SW	WC	3.85-29.60
Thallium	2-36	A	SSMS	-
	2.4-3	IE	INAA	10.9-11.2
	<0.20-1.40	SW	AAS	3.85-29.60
Tin	0.1-0.9	A	-	-
	1-47	A	SSMS	-
	<3-8	A	OES	6.15-18.27
	1-5	IE	-	-
	20	IE	SSMS	10.9-11.2
	<1-51	IE	OES	3.28-16.04
	<10	IW	OES	25.85
	0.6-1.6	IW	-	-
	<5-15	N	OES	11.29-15.83
	4-35	SW	SSMS	-
	<2-8	SW	OES	6.56-13.68
Titanium (wt %)	0.02-0.18	A	SSMS	-
	0.06-0.15	A	XRF	6.15-18.27
	0.05-0.17	IE	-	6.8-17.26
	0.07	IE	NAA	10.9
	0.02-0.15	IE	XRF	3.28-16.04
	0.08	IW	XRF	25.85
	0.06	N	XRF	11.29-15.83
	0.05-0.09	SW	SSMS	-
	0.03-0.13	SW	XRF	6.56-13.68
Uranium	0.3-1.0	A	SSMS	-
	0.09-3.70	SW	INAA	3.85-29.60

(continued)

TABLE 4 (continued). CONCENTRATIONS OF TRACE ELEMENTS IN COAL (5)

Element	Concn in whole coal (ppm)	Source	Analytical method	% Ash
Vanadium	19-25	A	-	-
	3-77	A	SSMS	-
	24-52	A	XRF/OES	6.15-18.27
	35	IE	-	-
	21-69	IE	INAA	10.9-11.2
	16-78	IE	XRF/OES	3.28-16.04
	40	IW	XRF/OES	25.85
	14-18	N	XRF/OES	11.29-15.83
	11-26	SW	XRF/OES	6.56-13.68
	2-8	SW	SSMS	-
	10-22.5	-	OES	-
	17-22	IW	-	-
Zinc	4.4-12	A	-	-
	3-80	A	SSMS	-
	21-40	A	AAS	6.15-18.27
	118-<3000	IE	-	6.8-17.26
	44	IE	-	-
	85-250	IE	SSMS	10.9-11.2
	10-5350	IE	AAS	3.28-16.04
	22-53	IW	-	-
	1444	IW	AAS	25.85
	59	N	-	-
	10-12	N	AAS	11.29-15.83
	1-17	SW	-	-
	4-26	SW	SSMS	-
	7-15	SW	AAS	6.56-13.68
	7.3	SW	XRF	6

a. Abbreviations for coal sources

A = Appalachian (Pennsylvania, Maryland, Virginia, West Virginia, Ohio, Eastern Kentucky, Tennessee, Alabama).

Av U.S. = A representative average for U.S. coals.

IE = Interior Eastern (Illinois, Indiana, Western Kentucky).

IW = Interior Western (Iowa, Missouri, Kansas, Oklahoma, Arkansas).

N = Northern Plains (Montana, North and South Dakota).

SW = Southwestern (Arizona, New Mexico, Colorado, Utah).

(continued)

TABLE 4 (continued). CONCENTRATIONS OF TRACE ELEMENTS IN COAL (5)

b. Abbreviations for analytical methods

AAS	=	Atomic Absorption Spectroscopy
AS	=	Absorption Spectroscopy
FAAS	=	Flameless Atomic Absorption Spectroscopy
GC-MES	=	Gas Chromatography with Microwave Emission Spectroscopic Detection
INAA	=	Instrumental Neutron Activation Analysis
ISE	=	Ion-Selective Electrodes
NAA	=	Neutron Activation with Radiochemical Separation
OES	=	Optical Emission Spectroscopy-Detection Method Unspecified
OES-DR	=	Optical Emission Spectroscopy with Direct Reading Detection
OES-P	=	Optical Emission Spectroscopy with Photographic Detection
PAA	=	Photon Activation Analysis
PES	=	Plasma Emission Spectroscopy
SSMS	=	Spark Source Mass Spectroscopy
SSMS-ID	=	Spark Source Mass Spectroscopy with Isotope Dilution
WC	=	Wet Chemistry
XRF	=	X-Ray Fluorescence Spectroscopy

TABLE 5. TRACE ELEMENTS IN ASHES OF COAL AND IN THE EARTH'S CRUST (19)

Element	Symbol	Maximum percentage in coal ashes	Average percentage of "rich" ashes	Percentage in earth's crust	Factor or enrichment	
					Maximum in coal ashes	Average of "rich" ashes
Beryllium.....	Be	0.1	0.03	0.0002 to 0.001	100 to 500	30 to 150
Boron.....	B	0.3	.06	0.0003	1,000	200
Scandium.....	Sc	0.04	.006	0.0003 to 0.0006	70 to 130	10 to 20
Cobalt.....	Co	0.15	.03	0.004	40	8
Nickel.....	Ni	0.8	.07	0.01	80	7
Zinc.....	Zn	1.	-	0.02	50	-
Gallium.....	Ga	0.04	.01	0.001 to 0.0015	30 to 40	7 to 10
Germanium.....	Ge	1.1	.05	0.0004 to 0.0007	1,600 to 2,800	70 to 120
Arsenic.....	As	0.8	.05	0.0005	1,600	100
Yttrium.....	Y	0.08	.01	0.001	80	10
Zirconium.....	Zr	0.5	-	0.02	25	-
Molybdenum.....	Mo	0.05	.02	0.0015	30	13
Antimony.....	Sb	0.1	.02	-	-	-
Tin.....	Sn	0.05	.02	0.005	10	4
Lead.....	Pb	0.1	-	0.0016	70	-
Bismuth.....	Bi	0.003	-	-	-	-
Silver.....	Ag	0.0005 to 0.001	.0002	0.00001	50 to 100	20
Gold.....	Au	0.00002 to 0.00005	-	0.0000005	40 to 100	-
Rhodium.....	Rh	0.000002	-	-	-	-
Palladium.....	Pd	0.00002	-	-	-	-
Platinum.....	Pt	0.00007	-	-	-	-

TABLE 6. ENRICHMENT OF ELEMENTS DURING DECAY OF OAK AND BEECH HUMUS; PERCENT OF ASH (19)

	B_2O_3	MnO	NiO	GeO_2	As_2O_5	Ag	Au
Mineral soil (sand)	0.0007	0.04	0.002	0.0005	-	-	-
Ash from fresh oak leaves	0.5 to 1.0	2.00[a]	0.005	0.0005	-	-	-
Ash from oak humus	0.02	0.24	0.01	0.007	-	0.0001	-
Ash from beech humus	0.003	0.14	0.01	0.007	0.05	0.0005	0.00002

[a]Ash from fresh beech leaves; in weathered leaves from previous year, 0.77 percent MnO.

TABLE 7. QUANTITATIVE ANALYSES (in ppm) FOR 13 TRACE ELEMENTS IN DRILL-CORE COAL SAMPLES, POWDER RIVER BASIN. (Blank space indicates analysis not completed at time of report preparation. (20)

Sample interval (ft)	Drill-core sample no.	ppm, coal							
		As	F	Hg	Sb	Se	Te	Tl	U
100-109	458	2.	40	0.035	0.92	<0.1	0.1	<0.2	<0.2
109-112	459	2.	30	0.082	0.62	0.4	0.1	<0.2	0.8
240-247	462	2.	10	0.037	0.08	<0.1	<0.02	<0.2	<0.2
231-232	463	3.	10	0.051	0.12	<0.1	0.02	<0.2	0.4
116-127	464	1.	30	0.044	0.04	0.2	<0.02	<0.2	<0.2
127-137	465	1.	20	0.030	0.04	<0.1	<0.02	<0.2	<0.2
137-140	466	3.	30	0.106	0.06	0.6	<0.02	<0.2	1.2
100-104	467	2.	30	0.035	0.08	<0.1	<0.02	<0.2	0.9
60-68	468	2.	60	0.049	0.04	0.5	0.1	<0.2	0.8
166-176	469	2.	10	0.099	<0.04	0.2	0.05	<0.2	<0.2
108-118	470	3.		0.043		0.6			0.9
216-226	471	4.		0.065		0.5			0.3
71-72	472	5.		0.039		0.9			0.5
80-88	473	3.		0.035		0.5			0.4
88-98	474	2.		0.021		0.3	Not determined	Not determined	<0.2
143-150	475	3.		0.058		1.0			<0.2
92-101	476	5.		0.181		1.5			1.7
101-106	477	3.		0.048		0.5			0.5
140-147	478	4.		0.028		0.6			0.3
100-110	479	4.		0.041		1.2			1.5
110-120	480	3.		0.035		0.3			0.4

(continued)

TABLE 7. QUANTITATIVE ANALYSES (in ppm) FOR 13 TRACE ELEMENTS IN DRILL-CORE COAL SAMPLES, POWDER RIVER BASIN (20) (continued) (Blank space indicates analysis not completed at time of report preparation.)

Sample interval (ft)	Drill-core sample no.	ppm, ash					Ash %
		Cd	Cu	Li	Pb	Zn	
100-109	458	-	335	27	-	185	3.20
109-112	459	1.5	385	130	275	180	6.80
240-247	462	<1.0	420	50	545	175	3.25
231-232	463	<1.0	605	93	1660	195	4.56
116-127	464	<1.0	245	31	300	83	4.56
127-137	465	<1.0	180	28	195	93	3.43
137-140	466	1.5	145	44	120	240	7.12
100-104	467	<1.0	100	50	100	185	6.92
60-68	468	1.5	130	43	105	350	8.16
166-176	469	<1.0	120	27	80	115	4.87
108-118	470	<1.0	140	33	140	72	8.08
216-226	471	1.0	224	34	420	100	7.30
71-72	472	1.0	316	16	220	160	6.42
80-88	473	<1.0	80	20	110	24	8.24
88-98	474	<1.0	90	11	130	32	5.40
143-150	475	<1.0	180	21	120	42	6.20
92-101	476	1.5	180	57	87	480	11.3
101-106	477	<1.0	105	27	100	122	5.67
140-147	478	<1.0	105	16	100	104	5.00
100-110	479	<1.0	92	45	79	232	14.8
110-120	480	<1.0	84	25	69	224	6.52

SECTION 6

PHYSICAL CHARACTERIZATION OF ASH

GENERAL

The ash residue resulting from the combustion of coal is primarily derived from the inorganic mineral matter in the coal. As Table 3 shows, different types (rank) of coal produce different quantities of ash, depending on the concentration of mineral matter in that type of coal. Generally, ash makes up from 3 to 30 percent of the coal.[18]

During the combustion of coal, the products formed are partitioned into three categories--bottom ash, flyash, and vapors. The bottom ash is that part of the residue which is fused into particles heavy enough to drop out of the furnace gas stream (air and combustion gases). These particles are collected in the bottom of the furnace. The flyash is that part of the ash which is entrained in the combustion gas leaving the boiler. While most of this flyash is collected in either mechanical collectors and/or electrostatic precipitators, a small quantity of this material may pass through the collectors and be discharged into the atmosphere. The vapor is that part of the coal material which is volatilized during combustion. Some of these vapors are discharged into the atmosphere; others condense onto the surface of flyash particles and may be collected in one of the flyash collectors. For the majority of elements found in coal, most of their quantity (95 percent or more) will be found in the ash fractions, while the remainder (5 percent or less) will be discharged into the atmosphere.[2] The quantity of vapors produced depends primarily on the temperature history of the combustion gases and the concentrations and properties of the various elements in the coal.

The distribution of the ash between the bottom ash and flyash fractions is a function of the burner type, the type of coal (ash fusion temperature), and the type of boiler bottom (wet or dry). The first factor, burner type, is especially significant in determining the distribution. The different methods of firing pulverized-coal boilers are shown in Figure 3, while Table 8 presents the relative distribution of bottom ash and flyash by boiler firing method. Stoker fired units emit the smallest proportion of flyash, and this flyash is relatively coarse. In a cyclone unit the melting point for the ash is exceeded, and 80-85 percent of the ash is then melted and collected as slag. The small quantity of flyash which a cyclone unit produces is usually composed of very fine particles (90 percent is smaller than 10 μm in diameter).[12] Pulverized coal units usually produce

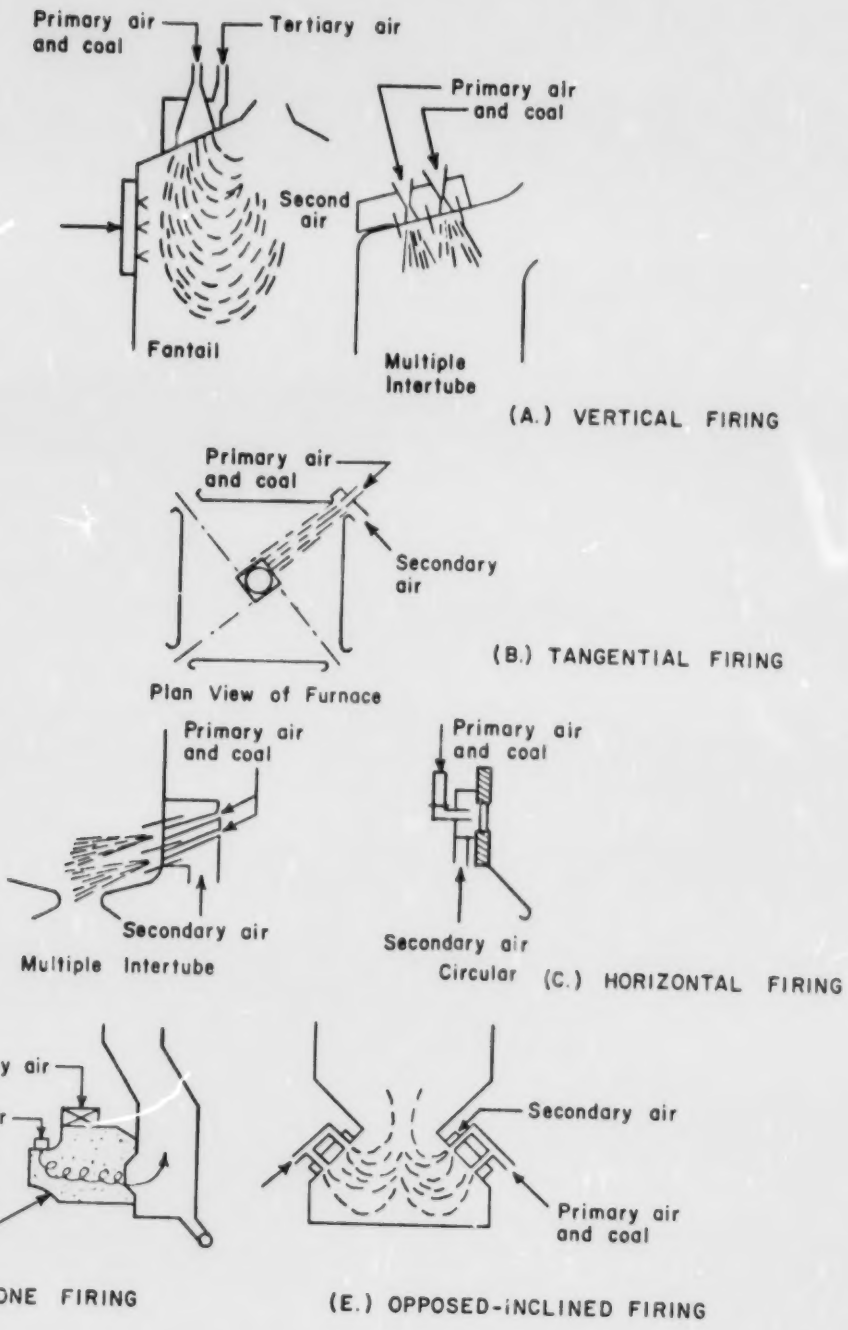

Figure 3. Pulverized-coal firing methods. (24)

TABLE 8. COMPARISON OF DISTRIBUTION BETWEEN BOTTOM ASH AND FLYASH BY TYPE OF BOILERS AND METHOD OF FIRING (21)

Wet (W) or dry (D) bottom boiler	Type of firing[a]	% Bottom Ash (typical)	% Fly Ash (typical)
W	PCFR	35	65
W	PCOP	35	65
W	PCTA	35	65
D	PCFR	15	85
D	PCOP	15	85
D	PCTA	15	85
-	CYCL	90	10
-	SPRE	35	65

[a]PCFR - Pulverized coal front firing
PCOP - Pulverized coal opposed firing
PCTA - Pulverized coal tangential firing
CYCL - Cyclone
SPRE - Spreader stoker

65 to 80 percent flyash[21] and 20 to 35 percent bottom ash. The second factor, ash fusion temperature, is important in that ashes with lower fusion temperatures tend to be melted within the boiler and collected as bottom ash. Finally, wet bottom boilers are designed to produce and process a much larger proportion of bottom ash than are dry bottom boilers.

The ashes vary in size as they are discharged from the furnace from less than one μ to 4 cm in diameter. The flyash fraction generally consists of fine spherical particulates usually ranging in diameter from 0.5 μ to 100 μ.[12,22] This fraction spans a color range of light tan to gray to black. Increased carbon content causes a darker gray-black tone, while increased iron content tends to produce a tan-colored ash. The pH of flyash contacted with water may vary from 3 to 12, with the pH for the majority of pulverized coal-burned flyashes contacted with water ranging from 8 to 12.[23]

Cenospheres, which are very lightweight particles that float on ash pond surfaces, are an interesting fraction of the flyash. These are silicate glass spheres filled with nitrogen and carbon dioxide which vary from 20 μ to 200 μ in diameter. Particle density ranges from 0.4 g/cc to 0.8 g/cc. These particles may comprise as much as 5 percent by weight or 20 percent by volume of the flyash.[12]

The bottom ash fraction of coal combustion residue is collected in either the ash or the slag form, depending on whether the boiler is a wet bottom or dry bottom design. Dry bottom boilers produce ash, which is composed usually of gray to black, angular particles with porous surfaces. Wet bottom boilers produce slag, which generally consists of angular black particles with a glassy appearance. A comparison of the grain size distribution curves for several bottom ash and flyash samples from pulverized coal units is given in Figure 4. These samples were taken from Fort Martin Unit 1 (tangentially-fired) and Unit 2 (wall-fired). These bottom ashes range from about 0.07 mm to 40 mm in diameter and the flyashes from 0.0015 mm to 0.45 mm in diameter.

For the collected flyash, particle size distribution and total surface area vary depending on the types of collector employed. A comparison of the particle size distribution of flyash collected in an electrostatic precipitator and that collected in a mechanical collector is shown in Figure 5. The ash collected by electrostatic precipitators contains a much greater percentage of the very small particles (<1.5μ). However, as the size of the particles approaches the 150 μ diameter, the percentages of ash collected by the two methods are approximately equal.[25]

The reliability of particle size distribution data also depends on the method employed to determine particle size. For example, data in Table 9 is a comparison between three methods (microscope count, turbidimeter, and hydrometer). Results from both the turbidimeter and the hydrometer indicate that the flyash contained a much lower percentage of the very fine particles than do the results of the microscope count method. The apparent low percentage of fine particles when analyzed by the turbidimeter and hydrometer was due to large differences in the specific gravity of the particles. The small

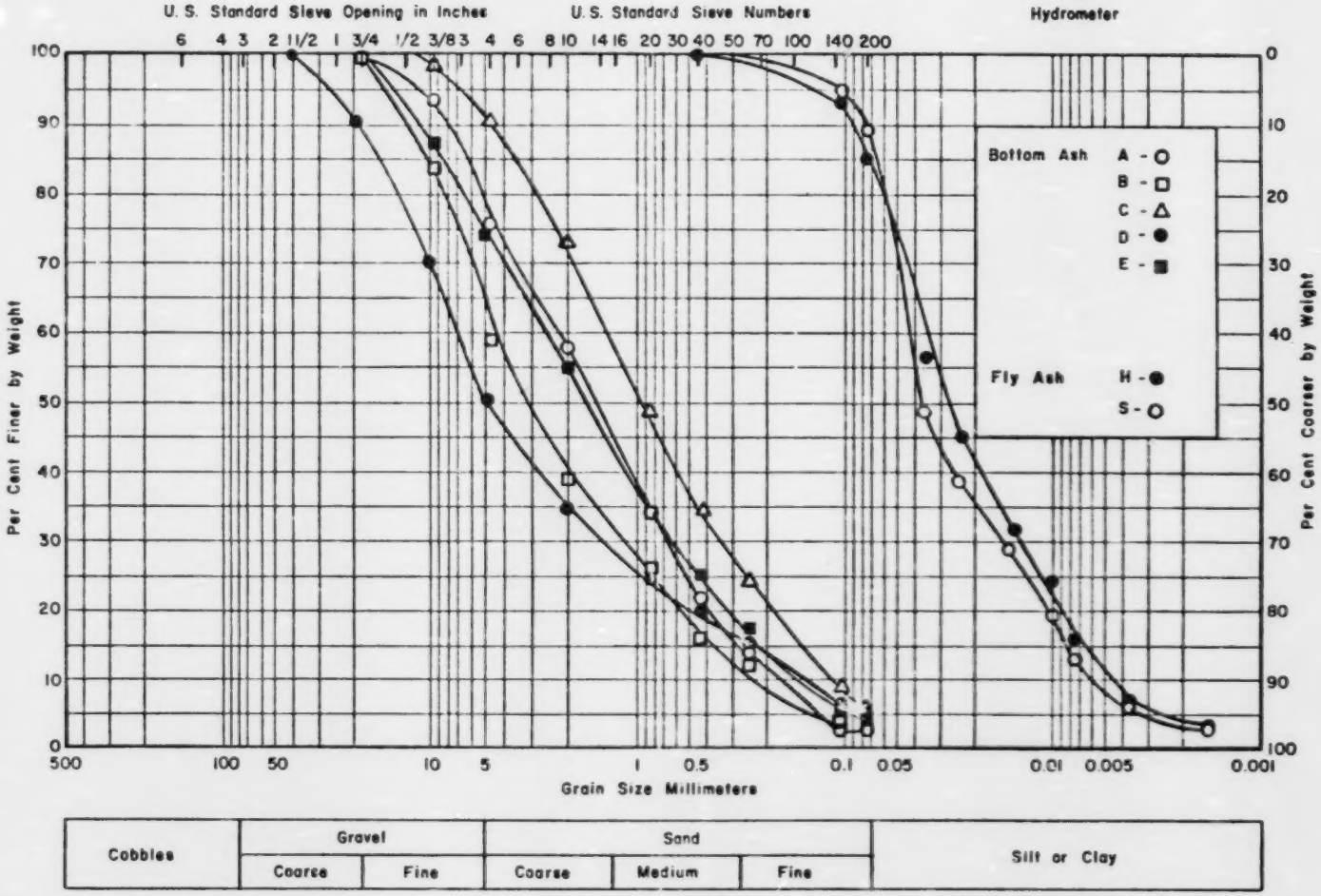
U. S. Standard Sieve Opening in Inches
6 4 3 2 1 1/2 1 3/4 1/2 3/8 3 4 6 8 10 14 16 20 30 40 50 70 100 140 200
U. S. Standard Sieve Numbers
Hydrometer
Per Cent Finer by Weight
Per Cent Coarser by Weight
Bottom Ash A - O
B - □
C - △
D - ●
E - ■
Fly Ash H - ●
S - O
500 100 50 10 5 1 0.5 0.1 0.05 0.01 0.005 0.001
Grain Size Millimeters
Cobbles
Gravel
Coarse
Fine
Sand
Coarse
Medium
Fine
Silt or Clay

Figure 4. Grain size distribution curves for bottom ash and flyash. (25)

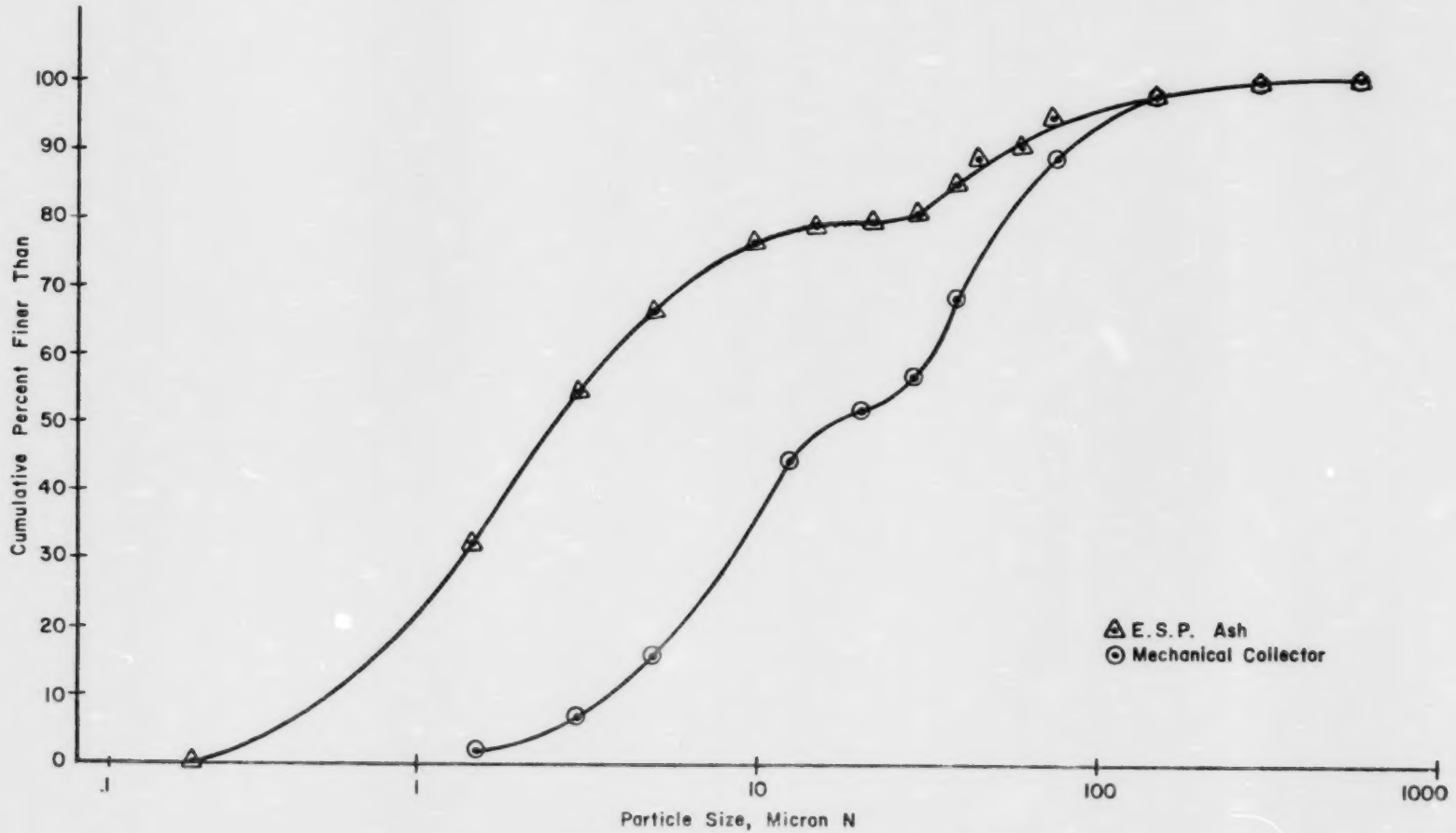

Figure 5. Particle size distribution of flyash. (26)

TABLE 9. COMPARISON OF PARTICLE SIZE DISTRIBUTION BY THREE METHODS OF DETERMINATION (26)

Cumulative percentage by weight finer than

Microscope Count			Turbidimeter			Hydrometer			
Size μ	MC	ESP	Size μ	MC	ESP	M.C. Size u	M.C. Percent	ESP Size u	ESP Percent
2380	100.0	---	60	80.6	91.2				
1190	99.9	---	55	76.1	89.5	58	90.0	59	94.1
590	99.5	100.0	50	71.5	87.9	43	81.0	42	90.0
297	98.8	99.4	45	67.6	85.6	33	70.5	31	83.4
149	97.5	98.0	40	61.6	82.2	25	59.0	23	74.2
74	88.0	93.7	35	54.9	79.3	15	12.0	14	13.8
60	81.6	91.3	30	46.3	73.1	12	3.4	11	10.8
45	72.3	87.7	25	36.0	64.9	--	--	7.5	8.3
38	68.2	85.4	20	24.9	51.6	--	--		
30	57.9	80.2	15	14.0	33.9				
23	51.4	79.0	10	4.8	24.6				
15	48.7	78.3	7.5	1.1	15.2				
10	37.6	76.0							
5	16.9	67.0							
3	7.3	55.6							
1.5	2.7	32.7							

MC - Mechanical Collector

ESP - Electrostatic Precipitator

particles with higher specific gravities tended to settle out very fast, indicating that they were much larger in size.[26] The different results sometimes obtained using different methods, indicate the need for improvement and standardization of methods for determining particle size.

COMPARISON OF ASH FROM A MECHANICAL COLLECTOR AND ELECTROSTATIC PRECIPITATOR

While it is recognized that all flyashes vary to some degree in their physical properties, the following description of two ashes (one collected by a mechanical collector and the other by an electrostatic precipitator) may illustrate the general or typical characteristics. These ashes were studied[26] by dividing the samples roughly into three fractions--coarse, medium, and fine—through the use of a mechanical air separator. Each of these fractions was then subjected to both physical and chemical analyses.

The results of the sieve analysis of the samples are given in Tables 10 and 11. The percentage of material finer than the No. 325 sieve is higher for the ash collected by the electrostatic precipitator than for the mechanically collected ash in all three size fractions. For the medium and fine fractions, the percentage of material retained on all sieves is higher for the mechanically collected ash than for the ash collected by the electrostatic precipitator. This is also true for the coarse fraction, except for the material retained on sieves No. 270 and 325.

The fineness (by three different methods) and the specific gravity of the three fractions are given in Table 12. The results of these tests indicate that coarser materials have higher specific gravities for both types of collection devices.

Table 13 presents the results of the chemical analysis for the physically size-differentiated fractions. The major differences noted in this analysis are as follows.[26]

1. The lithophile materials (alumino-silicates) were more concentrated in the finer fractions.
2. The magnetite-hematite materials (iron-bearing) were more concentrated in the coarser fractions.
3. The alkalies (Na and K) were generally more concentrated in the finer fractions. (This occurrence is probably because of their association with the lithophiles.)
4. The higher loss on ignition occurred in the finer fraction.

Representative samples of the ash were sieved across sieves Nos. 200, 325, 400, and 500. The fraction of each sample of flyash retained on each sieve was then subjected to petrographic analysis. The results of this analysis are shown in Table 14.

The glass constituent, which was the most abundant component in both samples, was more concentrated in the electrostatic precipitator ash. Also, the finer materials included a higher percentage of glass, with the material passing

TABLE 10. PARTICLE SIZE DISTRIBUTION OF ASH FROM A MECHANICAL COLLECTOR (26)

Classification	Weight		Particle Size Distribution (Tyler), % by Weight							
	lb	%	Retained on No. 48 Sieve	Passing No. 48 Retained on No. 65	Passing No. 65 Retained on No. 100	Passing No. 100 Retained on No. 150	Passing No. 150 Retained on No. 200	Passing No. 200 Retained on No. 270	Passing No. 270 Retained on No. 325	Finer than No. 325 Sieve
Coarse	6.5	3.7	17.8	6.3	12.0	17.3	24.0	13.9	6.5	2.2
Medium	47.5	27.0	0	0	0.9	3.8	13.0	19.6	27.9	34.8
Fine	122.0	69.3	0	0	0	0.2	0.6	1.4	4.4	93.4

TABLE 11. PARTICLE SIZE DISTRIBUTION OF ASH FROM AN ELECTROSTATIC PRECIPITATOR (26)

Classification	Weight		Particle Size Distribution (Tyler), % by Weight							
	lb	%	Retained on No. 48 Sieve	Passing No. 48 Retained on No. 65	Passing No. 65 Retained on No. 100	Passing No. 100 Retained on No. 150	Passing No. 150 Retained on No. 200	Passing No. 200 Retained on No. 270	Passing No. 270 Retained on No. 325	Finer than No. 325 Sieve
Coarse	11.5	1.9	7.5	2.9	7.5	9.4	23.8	16.5	15.2	17.2
Medium	52.0	8.7	0.3	0.3	1.2	2.8	10.0	15.1	19.7	50.6
Fine	534.0	89.4	0	0	0	0.1	0.2	0.5	1.2	98.0

TABLE 12. SURFACE AREA BY THREE METHODS (26)

Test Method	Results Obtained IN	MECHANICAL COLLECTED ASH				ESP COLLECTED ASH			
		As Received	Processed			As Received	Processed		
			Fine	Medium	Coarse		Fine	Medium	Coarse
Air Permeability	sq cm/g	1167	2457	709	418	3480	4215	1150	611
Turbidemeter	sq cm/g	720	1110	290	90	1570	2010	875	215
Hydrometer	sq cm/g	1079	2266	790	370	3126	4039	1216	848
Specific Gravity			2.47	2.60	2.92		2.53	2.64	3.02

TABLE 13. CHEMICAL ANALYSIS (26)

Test Result	MECHANICAL COLLECTED FLY ASH				ESP COLLECTED FLY ASH			
	As Received	Fine	Medium	Coarse	As Received	Fine	Medium	Coarse
SiO_2,%	41.57	44.65	37.57	33.08	44.29	46.38	36.40	26.72
Al_2O_3,%	18.53	18.19	14.19	13.05	17.94	18.36	15.48	9.53
Fe_2O_3,%	24.33	19.87	38.23	43.46	19.64	16.46	37.28	53.35
CaO,%	4.83	5.07	4.00	5.56	6.67	6.61	5.08	4.92
MgO,%	0.96	0.78	0.86	0.71	1.03	0.91	0.72	0.59
Sulfide sulfur, %	0.05	0.00	0.01	0.07	0.00	0.00	0.005	0.02
SO_3,%	0.64	0.70	0.42	0.76	2.40	2.60	0.87	0.74
Ignition loss, %	4.34	5.61	0.80	0.20	2.64	2.87	2.44	1.49
Na_2O,%	0.23	0.24	0.17	0.20	0.94	1.20	0.51	0.36
K_2O,%	1.96	2.10	1.54	1.23	1.90	2.03	1.20	0.86
Total alkalies as Na_2O,%	1.52	1.62	1.18	1.01	2.19	2.54	1.30	0.93
Total carbon, %	3.68	4.75	0.72	0.36	1.53	1.40	2.04	1.19
Moisture loss, %	0.28	0.26	0.08	0.11	0.43	0.65	0.24	0.18
Insoluble residue, %	84.40	82.92	89.26	73.82	75.68	75.72	87.13	83.99

TABLE 14. PHASE COMPOSITION (26)

Constituent	ESP COLLECTOR Percentage Retained on Sieves* No. 200	No. 325	No. 400	No. 500	Passing No. 500	Composition of Whole Sample %**	MECHANICAL COLLECTOR Percentage Retained on Sieves* No. 200	No. 325	No. 400	No. 500	Passing No. 500	Composition of Whole Sample %**
Glass	32	49	52	56	87	79	35	55	61	58	63	58
Magnetite-hematite	2	14	13	14	5	6	8	5	20	26	16	16
Carbon	33	8	9	5	1	4	47	29	7	8	5	13
Anisotropic material	27	22	18	15	3	6	3	3	3	3	5	4
Aggregates	6	7	8	10	4	5	7	8	9	5	11	9
Total	100	100	100	100	100	100	100	100	100	100	100	100

*Percentage is based on count of more than 300 particles in each sieve fraction.
**Percentage is based on gradation of as-received sample and on the distribution of constituents of wet sieved fractions.

the 500 mesh sieve containing the highest percentage of glass. "The glass consisted of colorless to light green and amber spheres, broken hollow spheres, ellipsoids, and teardrop--and irregularly shaped particles. Many contained inclusions of iron oxide, birefringent material, and small bubbles."[16] The birefringent material, which refracts light in two slightly different directions, was probably mullite in this case, since this mineral was identified by X-ray diffraction.

The magnetite-hematite material was more concentrated in the ash from the mechanical collector than it was in ash collected from the electrostatic precipitator. In both ashes, this material was the second most abundant constituent. These particles are spherically-shaped and have the characteristic of appearing opaque in transmitted light while exhibiting a gray metallic luster in reflected light. Magnetite-hematite particles may also be found as small opaque inclusions in the glass particles. In the 1-20 micron range, a few bright red hematite particles were observed.[26]

The carbon particles had varied shapes with the predominant shape being highly irregular cellular particles. These particles increased in abundance as the particle size increased. The carbon particles in the coarser ash had a cinder-like appearance and were magnetic due to particles of magnetite and hematite lodged in the cellular structure of their walls. The original woody structure was observed in a few particles.[16]

The anisotropic material was a low birefringent substance enclosed in glass particles and quartz in a well-crystallized state. The low birefringent material was a mixture of mullite and devitrified glass. In the finer ash, highly carbonated portland cement was found to be a contaminant of anisotropic material.[26]

The aggregates of glass, magnetite, hematite, and carbon particles were present in all size ranges. A few of these particles appeared to be fused, but the majority of them were very loosely held together. X-ray diffraction studies showed that the crystalline constituents were magnetite, hematite, quartz, mullite, portland cement, and traces of anhydrite ($CaSO_4$).[26]

SECTION 7

CHEMICAL CHARACTERIZATION OF ASH

CHEMICAL COMPOSITION BY COAL RANK AND BY ASH FRACTION

The chemical composition of coal ash depends largely on the geologic and geographic factors related to the coal deposit, the combustion conditions, and the removal efficiency of air pollution control devices. The inorganic constituents of ash are those typical of rocks and soils, primarily Si, Al, Fe, and Ca; the oxides of these four elements comprise 95 percent to 99 percent of the composition of ash. Ash also contains smaller amounts (0.5 percent - 3.5 percent) of Mg, Ti, S, Na, and K as well as very small quantities (parts per million) of from twenty to fifty elements.

One must use caution in attempting to characterize the effluents from a power plant based on the average ash analysis from coal of any given rank. As Table 15 illustrates, the maximums and minimums of some trace elements exhibit great variability within ashes from coals of the same rank. These values are from atomic absorption analyses of coals ashed in air at 600°C.

Analysis of various ashes shows that the distribution of major elements is approximately the same in the bottom ash and flyash fractions. However, for certain of the trace components, there is a very definite partitioning between the bottom ash and flyash. Table 16 shows that for some elements there can be differences of an order of magnitude in the concentrations of trace elements between these two fractions; for example, Se exhibits this tendency.

Results from several plants on the concentrations of trace elements in flyash or flue gas are shown in Table 17. The source of the coal, the control method, and the method used for analysis of the element are given whenever available.

ANALYTICAL STUDIES

The quantities of potentially hazardous pollutants entering the environment as the result of coal combustion increase with the steady growth in amount of coal being utilized. A lack of information concerning the trace constituents of coal during and after combustion has coupled with increased knowledge of possible pollutant effects to heighten awareness of this problem.

TABLE 15. RANGE IN AMOUNT OF TRACE ELEMENTS PRESENT IN COAL ASHES (27)
(ppm)

	Anthracites			High volatile bituminous		
Element	Max.	Min.	Average (5)	Max.	Min.	Average (24)
Ag	1	1	*	3	1	*
B	130	63	90	2800	90	770
Ba	1340	540	866	4660	210	1253
Be	11	6	9	60	4	17
Co	165	10	81 (4)	305	12	64
Cr	395	210	304	315	74	193
Cu	540	96	405	770	30	293
Ga	71	30	42	98	17	40
Ge	20	20	*	285	20	*
La	220	115	142	270	29	111
Mn	365	58	270	700	31	170
Ni	320	125	220	610	45	154
Pb	120	41	81	1500	32	183
Sc	82	50	61	78	7	32
Sn	4250	19	962	825	10	171 (22)
Sr	340	80	177	9600	170	1987
V	310	210	248	840	60	249
Y	120	70	106	285	29	102
Yb	12	5	8	15	3	10
Zn	350	155	*	1200	50	310 (14)
Zr	1200	370	688	1450	115	411

* = Insufficient figures to compute an average value.

O = Figures encircled indicate the number of samples used to compute average values.

(continued)

TABLE 15. RANGE IN AMOUNT OF TRACE ELEMENTS PRESENT IN COAL ASHES (27) (continued)

(ppm)

	Low Volatile Bituminous			Medium Volatile Bituminous		
Element	Max.	Min.	Average (8)	Max.	Min.	Average (7)
Ag	1.4	1	*	1	1	*
B	180	76	123	780	74	218
Ba	2700	96	740	1800	230	896
Be	40	6	16	31	4	13
Co	440	26	172	290	10	105(6)
Cr	490	120	221	230	36	169
Cu	850	76	379	560	130	313
Ga	135	10	41(7)	52	10	*
Ge	20	20	*	20	20	*
La	180	56	110	140	19	83
Mn	780	40	280	4400	125	1432
Ni	350	61	141	440	20	263(6)
Pb	170	23	89	210	52	96
Sc	155	15	50	110	7	56
Sn	230	10	92(7)	160	29	75
Sr	2500	66	818	1600	40	668
V	480	115	278	860	170	390
Y	460	37	152	340	37	151
Yb	23	4	10	13	4	9
Zn	550	62	231	460	50	195(6)
Zr	620	220	458	540	180	326

* = Insufficient figures to compute an average value.
O = Figures encircled indicate the number of samples used to compute an average value.

(continued)

TABLE 15. RANGE IN AMOUNT OF TRACE ELEMENTS PRESENT IN COAL ASHES (27) (continued) (ppm)

Lignites and Subbituminous

Element	Max.	Min.	Average (13)
Ag	50	1	*
B	1900	320	1020
Ba	13900	550	5027
Be	28	1	6
Co	310	11	45
Cr	140	11	54
Cu	3020	58	655
Ga	30	10	23 (12)
Ge	100	20	*
La	90	34	62
Mn	1030	310	688
Ni	420	20	129 8
Pb	165	20	60
Sc	58	2	18 (10)
Sn	660	10	156
Sr	8000	230	4660
V	250	20	125
Y	120	21	51
Yb	10	2	4
Zn	320	50	*
Zr	490	100	245

*=Insufficient figures to compute an average value.

O =Figures encircled indicate the number of samples used to compute average values.

TABLE 16. COMPARISON OF FLY ASH AND BOTTOM ASH FROM VARIOUS UTILITY PLANTS (2,28,29,30)

Compound or Element	Plant 1(30)		Plant 2(30)		Plant 3(30)		Plant 4(30)		Plant 5(29)		Plant 6(2,28)	
	FA	BA	FA	BA	FA	BA	FA	BA	FA	BA	FA	BA
SiO_2,%	59.	58.	57.	59.	43.	50.	54.	59.	NR	NR	42.	49.
Al_2O_3,%	27.	25.	20.	18.5	21.	17.	28.	24.	NR	NR	17.	19.
Fe_2O_3,%	3.8	4.0	5.8	9.0	5.6	5.5	3.4	3.3	20.4	30.4	17.3	16.0
CaO, %	3.8	4.3	5.7	4.8	17.0	13.0	3.7	3.5	3.2	4.9	3.5	6.4
SO_3, %	0.4	0.3	0.8	0.3	1.7	0.5	0.4	0.1	NR	0.4	NR	NR
MgO, %	0.96	0.88	1.15	0.92	2.23	1.61	1.29	1.17	NR	NR	1.76	2.06
Na_2O,%	1.88	1.77	1.61	1.01	1.44	0.64	0.38	0.43	NR	NR	1.36	0.67
K_2O, %	0.9	0.8	1.1	1.0	0.4	0.5	1.5	1.5	NR	NR	2.4	1.9
P_2O_5,%	0.13	0.06	0.04	0.05	0.70	0.30	1.00	0.75	NR	NR	NR	NR
T_1O_2,%	0.43	0.62	1.17	0.67	1.17	0.50	0.83	0.50	NR	NR	1.00	0.68
As,ppm	12.	1.	8.	1.	15.	3.	6.	2.	8.4	5.8	110.	18.
Be ,ppm	4.3	3.	7.	7.	3.	2.	7.	5.	8.0	7.3	NR	NR
Cd,ppm	0.5	0.5	0.5	0.5	0.5	0.5	1.0	1.0	6.44	1.08	8.0	1.1
Cr,ppm	20.	15.	50.	30.	150.	70.	30.	30.	206.	124.	300.	152.
Cu,ppm	54.	37.	128.	48.	69.	33.	75.	40.	68.	48.	140.	20.
Hg,ppm	0.07	0.01	0.01	0.01	0.03	0.01	0.08	0.01	20.0	0.51	0.05	0.028
Mn,ppm	267.	366.	150.	700.	150.	150.	100.	100.	249.	229.	298.	295.
Ni,ppm	10.	10.	50.	22.	70.	15.	20.	10.	134.	62.	207.	85.
Pb,ppm	70.	27.	30.	30.	30.	20.	70.	30.	32.	8.1	80.	6.2
Se,ppm	6.9	0.2	7.9	0.7	18.0	1.0	12.0	1.0	26.5	5.6	25.	0.08
V ,ppm	90.	70.	150.	85.	150.	70.	100.	70.	341.	353.	440.	260.
Zn,ppm	63.	24.	50.	30.	71.	27.	103.	45.	352.	150.	740.	100.
B ,ppm	266.	143.	200.	125.	300.	70.	700.	300.	NR	NR	NR	NR
Co,ppm	7.	7.	20.	12.	15.	7.	15.	7.	6.0	3.6	39.	20.8
F ,ppm	140.	50.	100.	50.	610.	100.	250.	85.	624.	10.6	NR	NR

TABLE 17. CONCENTRATIONS OF TRACE ELEMENTS IN COAL FLY ASH AND FLUE GAS (5)
(ppm)

Element	Concn in coal	Source[a]	Control method[b]	Concn in fly ash		Concn suspended in flue gas		Analytical method
				Before control	After control	Before control	After control	
Antimony	-	A	ESP	-	-	265	58	OES-P
	<700	IE	Mech	<600	<600	-	-	-
	-	IE	ESP	-	-	689	6.8	AAS
	-	IE	Cy	-	17-53	-	-	SSMS
	0.72-1.4	-	ESP	-	-	-	1.7±0.5	INAA
	-	SW	ESP	-	18	-	-	XRF
	-	SW	WS	14	22	-	-	XRF
	0.5	IE	ESP	12	55	-	-	INAA
Arsenic	5.44	Av U.S.	-	-	147	-	-	OES
	-	A	ESP	-	-	414	193	OES-P
	-	A	ESP	-	-	1513	47	OES-P
	-	IE	Cy	-	680-1700	-	-	AAS
	20-32	-	ESP	-	-	-	72±18	PAA
	-	SW	ESP	-	150	-	-	XRF
	-	SW	WS	130	280	-	-	XRF
	14	IE	ESP	120	440	-	-	INAA
Barium	-	A	ESP	-	-	1644	26	OES-P
	<300	IE	Mech	<400	<400	-	-	-
	130-210	-	ESP	-	-	-	72 ±44	INAA
	59	IE	ESP	450	750	-	-	INAA
Beryllium	-	A	ESP	-	-	32	6	OES-P
	<2	IE	Mech	10	10	-	-	-
	-	IE	Cy	-	34-60	-	-	OES
	<5	IE	ESP	3-17	<10	-	-	SSMS
Boron	-	A	ESP	-	-	1573	66	OES-P
	100-200	IE	ESP	250-3000	150-300	-	-	SSMS
Bromine	32-45	-	ESP	-	-	-	2.2±0.5	INAA
Cadmium	-	-	ESP	-	<20-170	-	-	OES
	-	A	ESP	-	-	232	54.5	OES-P
	6	IE	Mech	160	20	-	-	-
	-	IE	ESP	-	-	8.5	0.1	FAAS
	-	IE	Cy	-	13-35	-	-	AAS
	0.46	IE	ESP	8.0	51	-	-	SSMS-ID
Chlorine	355-407	IE	ESP	<5-50	1000	-	-	INAA

(continued)

TABLE 17. (continued). CONCENTRATIONS OF TRACE ELEMENTS IN COAL FLY ASH AND FLUE GAS (5)

(ppm)

Element	Concn in coal	Source[a]	Control method[b]	Concn in fly ash: Before control	Concn in fly ash: After control	Concn suspended in flue gas: Before control	Concn suspended in flue gas: After control	Analytical method
Chromium	-	A	ESP	-	-	1674	20	OES-P
	20	IE	Mech	500	7400	-	-	-
	-	IE	ESP	-	-	300	0.7	FAAS
	-	IE	Cy	-	290-3300	-	-	AAS
	25-35	-	ESP	-	-	-	13.8±5.1	INAA
	20	IE	ESP	310	900	-	-	INAA
Cobalt	-	A	ESP	-	-	227	20	OES-P
	0	IE	Mech	60	70	-	-	-
	-	IE	Cy	-	60-130	-	-	OES
	4.9-6.2	-	ESP	-	-	-	3.4±2.1	INAA
	3.0	IE	ESP	41	65	-	-	INAA
Copper	-	A	ESP	-	-	620	48	OES-P
	20	IE	Mech	100	200	-	-	-
	-	IE	Cy	-	270-390	-	-	SSMS
	9.6	SW	ESP	-	320	-	-	XRF
	9.6	SW	WS	280	290	-	-	XRF
	50-100	IE	ESP	300-400	200-400	-	-	SSMS
Fluorine	<2-60	-	-	<10-100	-	-	-	SSMS
Iodine	25-64	-	ESP	-	-	-	28.3±3.1	INAA
Lead	-	A	ESP	-	-	649	94	OES-P
	<30	IE	Mech	200	200	-	-	-
	-	IE	Cy	-	1100-1600	-	-	AAS
	6.5-12.4	-	ESP	-	-	-	13.8±2.8	PAA
	-	SW	ESP	-	130	-	-	XRF
	-	SW	WS	110	340	-	-	XRF
	4.9	IE	ESP	80	650	-	-	SSMS-ID
Manganese	-	-	ESP	-	465	-	-	OES
	-	A	ESP	-	-	1362	23	OES-P
	90	IE	Mech	500	800	-	-	-
	-	IE	Cy	-	150-470	-	-	OES
	31-45	-	ESP	-	-	-	25±13	INAA
	34	IE	ESP	290	430	-	-	INAA
Mercury	0.11 0.63	SE	Mech[d]	-	-	-	62	FASS
	0.11-0.63	SE	ESP	-	-	-	43	FASS
	0.33	-	ESP	-	0.4	-	31	INAA/ASV/PES
	-	A	ESP	-	-	89	15	OES-P
	<2	IE	Mech	<0.2	20	-	-	-
	0.122	IE	ESP	0.05	-	-	-	FASS

(continued)

TABLE 17 (continued). CONCENTRATIONS OF TRACE ELEMENTS IN COAL FLY ASH AND FLUE GAS(5)

(ppm)

Element	Concn in coal	Source[a]	Control method[b]	Concn in fly ash: Before control	Concn in fly ash: After control	Concn suspended in flue gas: Before control	Concn suspended in flue gas: After control	Analytical method[c]
Molybdenum	-	A	ESP	-	-	181	13	OES-P
	<20	IE	Mech	<30	<30	-	-	-
	0.99	SW	ESP	-	60	-	-	XRF/WC
	0.99	SW	WS	54	110	-	-	XRF/WC
	3.6	IE	ESP	118	-	-	-	INAA
Nickel	10-30	-	ESP	-	50-290	-	-	OES
	-	A	-	-	-	792	18	OES-P
	90	IE	Mech	500	2000	-	-	-
	-	IE	ESP	-	-	395	1.3	FAAS
	-	IE	Cy	-	460-1600	-	-	AAS
	21-42	-	ESP	-	-	-	15.4±6.1	FAA
	<100-150	IE	ESP	500-1000	500-1000	-	-	SSMS
Selenium	<600	IE	Mech	<500	<500	-	-	-
	-	IE	ESP	-	-	114	6.5	INAA
	-	IE	Cy	-	11-59	-	-	FAAS
	2.8-7.8	-	ESP	-	-	-	12±5	INAA
	1.9	SW	ESP	73	62	-	-	XRF
	1.9	SW	WS	73	440	-	-	XRF
	2.2	IE	ESP	25	88	-	-	GC-MES
Tellurium	1-3	IE	ESP	<1-10	<1-10	-	-	SSMS
Thallium	<100	IE	Mech	100	50	-	-	-
	-	IE	Cy	-	29-76	-	-	SSMS
	2	IE	ESP	40-100	30	-	-	SSMS
Tin	-	A	ESP	-	-	570	61	OES-P
	<700	IE	Mech	<600	<600	-	-	-
	-	IE	Cy	-	7-19	-	-	SSMS
	20	IE	ESP	20	20	-	-	SSMS
Titanium	-	A	ESP	-	-	16320	264	OES-P
	<980	IE	Mech	5800	6600	-	-	-
	-	IE	Cy	-	9200-15900	-	-	XRF
	900-1450	IE	ESP	-	-	-	480±260	INAA
	510	IE	ESP	6080	10000	-	-	INAA

(continued)

TABLE 17 (continued). CONCENTRATIONS OF TRACE ELEMENTS IN COAL FLY ASH AND FLUE GAS (5)

(ppm)

Element	Conc in coal	Source[a]	Control method[b]	Concn in fly ash		Concn suspended in flue gas		Analytical method[c]
				Before control	After control	Before control	After control	
Vanadium	22.5	-	ESP/WS	116	-	-	-	OES
	-	A	ESP	-	-	2842	14	OES-P
	<200	IE	Mech	200	300	-	-	-
	-	IE	ESP	-	-	970	1.5	FAAS
	-	IE	Cy	-	150-480	-	-	SSMS
	37-46	-	ESP	-	-	-	27±32	INAA
	28.5	IE	ESP	440	1180	-	-	INAA
Zinc	1100	IE	Mech	5900	900	-	-	-
	-	IE	ESP	-	-	162	0.7	AAS
	55-110	-	ESP	-	-	-	43±23	INAA
	-	IE	Cy	-	8100-13000	-	11340-18200	SSMS
	7.3	SW	ESP	-	370	-	-	FAAS
	7.3	SW	WS	360	600	-	-	FAAS
	46	IE	ESP	740	5900	-	-	SSMS-ID

a. Control equipment:
Mech = Mechanical collector
Cy = Cyclone collector
ESP = Electrostatic precipitator
WS = Wet scrubber

b. Sample was collected upstream from the mechanical collector.

c. Abbreviations for analytical methods.

OES = Optical Emission Spectroscopy-Detection Method Unspecified
OES-P = Optical Emission Spectroscopy with Photographic Detection
FAAS = Flameless Atomic Absorption Spectroscopy
SSMS = Spark Source Mass Spectroscopy
INAA = Instrumental Neutron Activation Analysis
AAS = Atomic Absorption Spectroscopy
SSMS-ID = Spark Source Mass Spectroscopy with Isotope Dilution

Therefore, several studies have been made in recent years to determine the fate of potentially hazardous elements in the coal and ash. The studies which have been made to date concern the following locations.

1. A power plant in Illinois[3]
2. A midwestern power plant[4]
3. Chalk Point Station of the Potomac Electric Power Company[5,31]
4. Valmont Station of the Public Service Company of Colorado[6,32]
5. Allen Steam Plant of the Tennessee Valley Authority[2]
6. A Canadian steam-electric generating plant[33]
7. Three Northern Great Plains plants[7-10]
8. Widows Creek Steam Plant of the Tennessee Valley Authority[29]

The most significant result from these studies is that their conclusions concerning the potential pollutants were consistent, even though the studies were made on different sizes and types of systems with respect to megawatt output, furnace type, and collector configuration. These studies all indicate that certain potentially hazardous elements in coal (for example, arsenic, beryllium, cadmium, lead, and selenium)[5] are concentrated in or on the small flyash particles, while certain others, such as mercury, are emitted primarily as vapors. The following are brief summaries of these studies.

Illinois Power Plant[3]

This study focused on a 105-megawatt (MW) plant using 60 tons of coal per hour. While the method of firing was unspecified, the flyash collection device was an electrostatic precipitator (ESP) with a rated efficiency of 97.7 percent. The separation of the particles into size classes was accomplished by means of an in-stack cascade impactor which utilized aluminum discs as collection surfaces. Inlet and outlet samples from the ESP were analyzed by neutron activation for Fe, V, Cr, Ni, Mn, Pb, Sb, Cd, Zn, and Se.

It was reported that, of the elements emitted from the electrostatic precipitator, those concentrated in particulates in the submicron diameter range were antimony, chromium, lead, selenium, and zinc. Nickel was more greatly enriched in particulates in the 5-10 micron diameter range. The method of analysis for all of the elements, except selenium, was graphite furnace atomic absorption spectrophotometry. Selenium was determined by neutron activation analysis. Potential sources of error were felt to be related to problems with the sampling methodology, such as particle reentrainment, calibration inaccuracies, and wall loss effects. Wall losses were believed to be the most serious error, since they can range from 30-50 percent of the total amount collected.

Midwestern Power Plant[4]

Neither size (output) of the unit nor the type of furnace was specified in this report. The system utilized a cyclone collector for the flyash, and

the coal burned was from southern Indiana. The purpose of this study was to characterize the ash collected in the collector and the ash that passed the collector. The ash from the collector hoppers was size-differentiated physically in the laboratory by sieving and by aerodynamic separation. The flyash passing the collector was sampled in situ using an Andersen stack sampler. However, since the researcher failed to use a backup filter in this sampler, the particles less than 0.5 micron in diameter were not collected.

The following conclusions were derived from this study.

1. The concentration of trace elements in the ash is dependent on particle size. Generally, increasing concentrations are correlated with decreasing particle size (see Tables 18, 19, and 20).
2. There is a definite enrichment of certain elements in the smallest particles emitted from a power plant. These elements include lead, thallium, antimony, cadmium, selenium, arsenic, nickel, chromium, zinc, and sulfur.
3. The highest concentrations of the trace constituents occur in particulates in the 0.5 - 10.0 micron diameter range, the size of particulate that can be inhaled and deposited in the pulmonary region of the respiratory system.
4. Presently available emission control devices for fine particulates are less effective for removing particulates in the size range that contains the most toxic elements.

The theory advanced for this concentration of potentially toxic constituents in fine particles involved the volatilization of elements in the high-temperature zone of the boiler and preferential condensation of these elements or their compounds onto the surface of fine flyash particles in the cooler zones of the system. The methods used to perform the chemical analysis in this study were direct current arc emission spectroscopy, atomic absorption spectrometry, X-ray fluorescence spectrometry, and spark source mass spectrometry.

Chalk Point Station[5,31]

This study involved sampling at two 355-MW units, each of which burned 116 tons per hour of pulverized coal. The samples collected were coal, bottom ash, flyash from the economizer, flyash from the electrostatic precipitator, flyash suspended in stack gas, and particles collected from surrounding atmosphere. A cascade impactor with seven stages and a backup filter was used to collect the flyash in the stack. The analysis for the 35 elements under consideration was conducted by instrumental photon and neutron activation methods.

Values were determined for several types of enrichment factors, including the following:

1. The enrichment of an element in the coal relative to its abundance in the earth's crust.

TABLE 18. ELEMENTS SHOWING PRONOUNCED CONCENTRATION TRENDS WITH DECREASING PARTICLE SIZE (ppm unless otherwise noted) (4)

Particle diam, μ	Pb	Tl	Sb	Cd	Se	As	Ni	Cr	Zn	S, wt%	Mass Frac %
A. Fly Ash Retained in Plant											
Sieved fractions											
74	140	7	1.5	10	12	180	100	100	500	...	66.30
44-74	160	9	7	10	20	500	140	90	411	1.3	22.89
Aerodynamically sized fractions											
40	90	5	8	10	15	120	300	70	730	0.01	2.50
30-40	300	5	9	10	15	160	130	140	570	0.01	3.54
20-30	430	9	8	10	15	200	160	150	480	...	3.25
15-20	520	12	19	10	30	300	200	170	720	...	0.80
10-15	430	15	12	10	30	400	210	170	770	4.4	0.31
5-10	820	20	25	10	50	800	230	160	1100	7.8	0.33
5	980	45	31	10	50	370	260	130	1400	...	0.08
Analytical method	a	a	a	a	a	a	b		a	a	
B. Airborne Fly Ash											
11.3	1100	29	17	13	13	680	460	740	8100	8.3	
7.3-11.3	1200	40	27	15	11	800	400	290	9000	...	
4.7-7.3	1500	62	34	18	16	1000	440	460	6600	7.9	
3.3-4.7	1550	67	34	22	16	900	540	470	3800	...	
2.1-3.3	1500	65	37	26	19	1200	900	1500	15000	25.0	
1.1-2.1	1600	76	53	35	59	1700	1000	3300	13000	...	
0.65-1.1	...	...	...	...	...	...	...	...	...	48.8	
Analytical method	d	a	a	d	d	d	d	d	a	c	

(a) Dc arc emission spectrometry. (b) Atomic absorption spectrometry.
(c) X-ray fluorescence spectrometry. (d) Spark source mass spectrometry.

TABLE 19. ELEMENTS SHOWING LIMITED CONCENTRATION TRENDS WITH DECREASING PARTICLE SIZE (ppm unless otherwise noted) (4)

Particle diameter, μ	Fe, wt %	Mn	V	Si, wt %	Mg, wt %	C, wt %	Be	Al, wt %
A. Fly Ash Retained in Plant								
Sieved fractions								
74	...	700	150	...	...	...	12	...
44-74	18	600	260	18	0.39	11	12	9.4
Aerodynamically sized fractions								
40	50	150	250	3.0	0.02	0.12	7.5	1.3
30-40	18	630	190	14	0.31	0.21	18	6.9
20-30	...	270	340	...	...	0.63	21	...
15-20	...	210	320	...	...	2.5	22	...
10-15	6.6	160	320	19	0.16	6.6	22	9.8
5-10	8.6	210	330	26	0.39	5.5	24	13
5	...	180	320	...	...	...	24	...
Analytical method	a	b	a	d	d	d		d
B. Airborne Fly Ash								
11.3	13	150	150	34	0.89	0.66	34	19.7
7.3-11.3	...	210	240	...	...	0.70	40	...
4.7-7.3	12	230	420	27	0.95	0.62	32	16.2
3.3-4.7	...	200	230	...	...	0.57	55	...
2.06-3.3	17	240	310	35	1.4	0.81	43	21.0
1.06-2.06	...	470	480	...	...	0.61	60	...
0.65-1.06	15	...	...	23	0.19	...	...	9.8
Analytical method	d	b	c	d	d	e	b	d

(a)Dc arc emission spectrometry.(b)X-ray fluorescence spectrometry.
(c)Atomic absorption.(d)Spark source mass spectrometry. e Oxygen fusion.

TABLE 20. ELEMENTS SHOWING NO CONCENTRATION TRENDS
(ppm unless otherwise noted) (4)

Particle Diameter μm	Bi	Sn	Cu	Co	Ti	Ca	K
			A. Fly Ash Retained in Plant Sieved Fractions				
>74	>2	>2	120	28	...	...	...
44-74	>2	>2	260	27	0.61	5.4	1.2
			Aerodynamically Sized				
>40	>2	>2	220	75	0.91	2.5	2.54
30-40	>2	>2	120	76	0.64	6.3	6.26
20-30	>2	>2	160	55	...	...	...
15-20	>2	>2	220	50	...	4.5	4.46
10-15	>2	>2	220	55	0.66	4.0	4.04
5-10	>2	>2	390	46	1.09	...	...
>5	>2	>2	490	54	...	...	...
			B. Airborne Material				
>11.3	>1.7	7	270	60	1.12	4.9	4.9
7.3-11.3	>3.5	11	390	85	...	...	...
4.7-7.3	>4.0	18	380	90	0.92	4.2	4.2
3.3-4.7	>4.8	19	...	95	...	...	...
2.06-3.3	>4.5	16	330	90	1.59	5.0	5.0
1.06-2.06	>4.4	18	300	130	...	...	...
0.65-1.06	...	...	...	...	1.08	2.6	2.6

2. The enrichment of the elements in the collected flyash relative to the concentrations of these elements in the coal.
3. The enrichment factors for coal as a function of particle size distribution.
4. The enrichment of an element in the suspended flyash relative to its concentration in the coal.

The values for this last type of enrichment factor are shown in Figure 6. The conclusions from this study agreed with those of the previous study with respect to partitioning of the elements. Another conclusion regarded the enrichment of elements in urban aerosols. "Enrichment factors for coal combustion were compared with calculated enrichment factors for urban aerosols collected in Boston, Northwest Indiana, and San Francisco. The enrichment found in coal combustion products was not high enough to account for the high enrichment factors of elements such as antimony, arsenic, selenium, and zinc in urban aerosols."[5]

Valmont Power Station[6,32]

This study was made on a 180-MW unit employing a corner firing method. The particulate emission control system consisted of a mechanical collector followed by an electrostatic precipitator in parallel with a wet scrubber. The samples collected were for all input streams and all outfall streams. (See Figure 7 for sample points and flow rates.) Analytical methods used to determine concentrations were wet chemistry, atomic absorption spectrophotometry, and X-ray fluorescence spectrometry. Results of the chemical analysis of the various streams are given in Table 21.

The enrichment ratios for the trace elements in each sample were calculated relative to the concentration of aluminum in the sample. Aluminum was used as the basis for comparison because it is essentially nonvolatile at the temperatures in the furnace. The results showed that the concentrations of aluminum, iron, rubidium, strontium, yttrium, and niobium were approximately constant in all of the outlet ashes. On the other hand, concentrations of copper, zinc, arsenic, lead, and antimony were lowest in the bottom ash. The concentrations of each of these elements increased progressively in the flyash samples collected going downstream toward the stack. Based on the volatilization-condensation postulation explaining the increasing downstream concentration of these elements, a mathematical model was developed in which enrichment ratio was a function of the mass fraction of an element volatilized in the furnace, the specific surface area of each ash stream, and the total mass flow ratio of each ash stream.

The mass balance or imbalance closures for 16 elements are given in Table 22. KaaKinen et al. believed that the imbalances may have been due to one or more of the following factors.

1. Unsteady state conditions.
2. Sources and/or sinks of elements within the boundary of the mass balance.

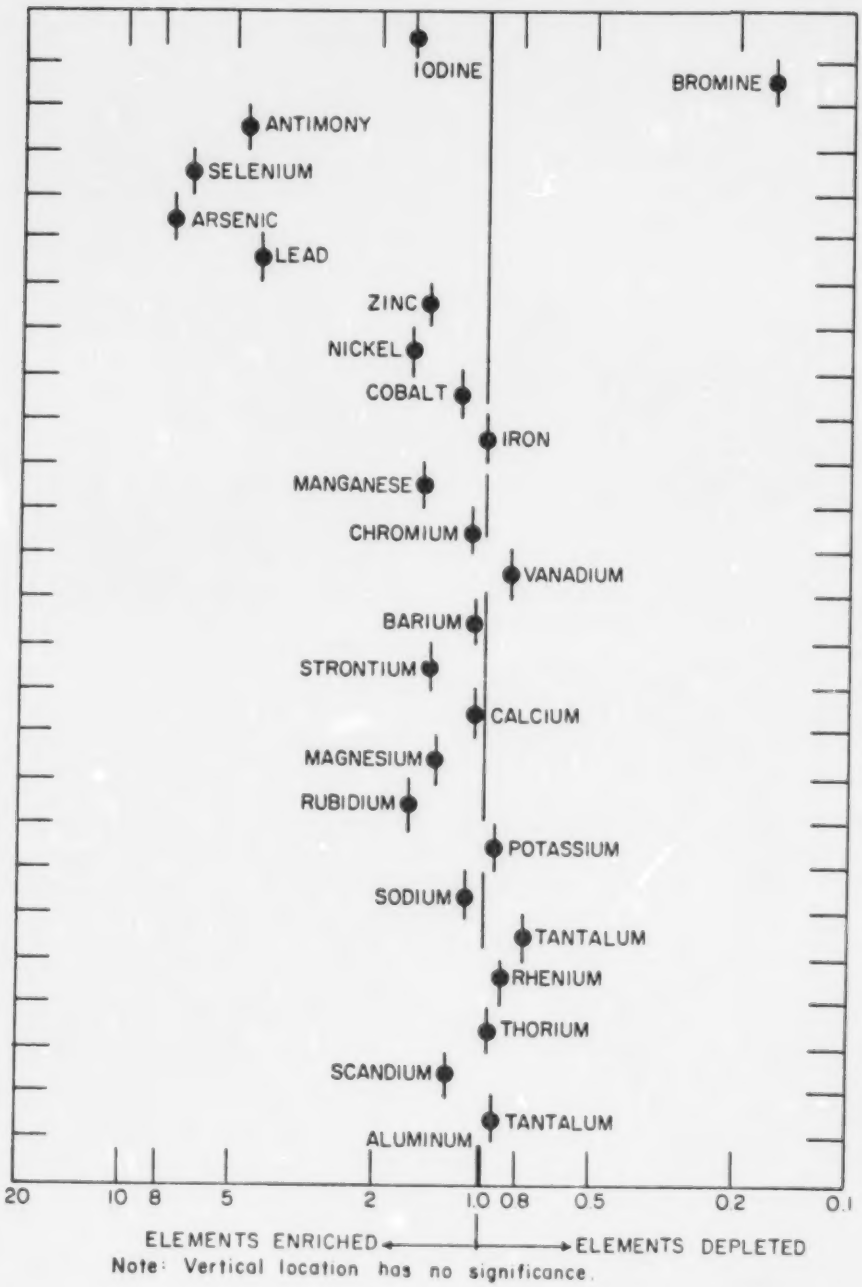

Figure 6. Enrichment factors of various elements on suspended particles in the stack with respect to the concentrations in the coal. (31)

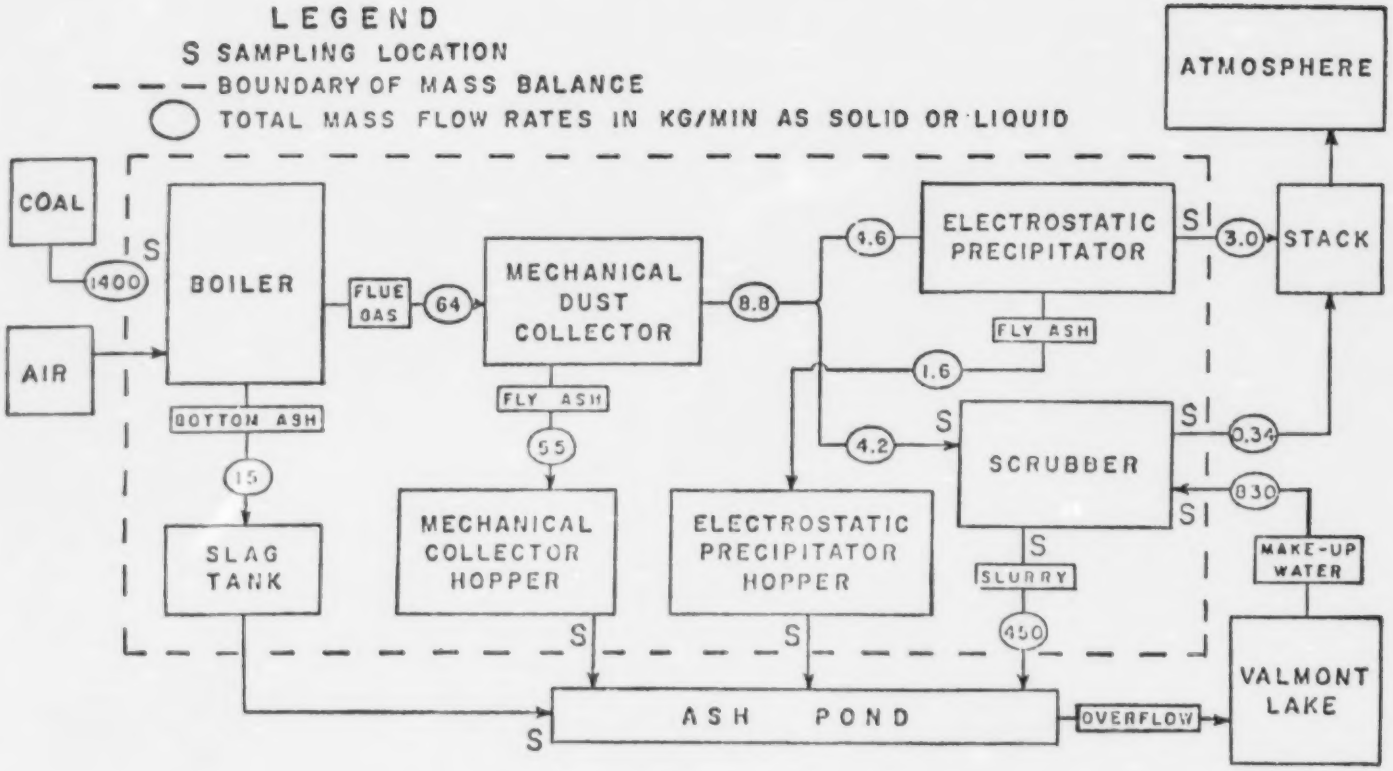

Figure 7. Sample points and flow rates for Valmont, unit no. 5. (6)

TABLE 21. TRACE ELEMENTS IN PLANT SAMPLES FROM VALMONT POWER STATION UNIT NO. 5 (6)
Concentration (ppm unless otherwise noted)

Element	Coal	Bottom ash	Mechanical collector hopper ash	Precipitator hopper ash	Scrubber inlet fly ash	Precipitator outlet fly ash	Scrubber outlet fly ash	Scrubber slurry	Analytical method
Aluminum[a]	0.49	8.8	9.6	10.2	9.0	9.2	7.4	0.10	AAS
Iron[a]	0.37	6.6	7.0	6.9	7.4	7.4	4.9	0.063	AAS
Copper	9.6	82	150	230	280	320	290	2.4	XRF
Zinc	7.3	58	100	250	360	370	600	2.2	XRF
Arsenic	-	15	44	120	130	150	280	1.1	XRF
Rubidium	2.9	48	50	73	51	56	28	0.50	XRF
Strontium	120	1800	2400	2500	2200	2500	2500	21	XRF
Yttrium	3.0	44	61	68	52	60	31	0.49	XRF
Niobium	0.76	12	16	19	17	19	18	0.49	XRF
Zirconium	13	220	260	210	160	190	80	1.8	XRF
Molybdenum	0.99	3.5	12	41	54	60	110	0.53	XRF/WC
Antimony	-	2.8	4.7	14	14	18	22	0.10	XRF
Lead	-	<5	13	66	110	130	340	0.91	XRF
Selenium	1.9	7.7	4.1	27	73	62	440	0.33	XRF
Mercury	0.070	0.140	0.026	0.310	-	-	-	0.014	FAAS

[a]Concentrations in wt. %.

TABLE 22. CLOSURE OF MASS BALANCE (6)

Element	Analytical Method	Relative Imbalance (%) Based on analyses of ashed coal	Based on analyses of whole coal
Mo	Color.	+10	
Mo	XF	- 4	
Fe	AA	- 7	
Fe	XF	-13	-18
Rb	XF	-25	-35[a]
Sr	XF	-17	-17
Y	XF	- 7	-15
Zr	XF	-20	-38
Nb	XF	-16	-13[a]
^{210}Pb	Rad.	+23	
^{210}Po	Rad.	+21	
Cu	XF	+11	+70[a]
Zn	XF	+ 9	+55[a]
As	XF	- 1[a]	+46[a]
Se	XF	-220[a]	+62
Sn	XF	+45[a]	+88[a]
Pb	XF	+13[a]	
^{226}Ra	Rad.	-60[a]	

[a] Values involving analyses for which inaccuracies or imprecisions are indicated to be a problem.

3. Analytical errors in concentration values.
4. Errors in total mass flow rate estimates.

The researchers felt that in this case factors (1) and (2) were probably insignificant while factors (3) and (4) could explain the observed imbalances.[32]

Allen Steam Plant[2,28,34,35]

A study was made at the Tennessee Valley Authority's Allen Steam Plant which included the sampling of all input streams, outfall streams, and environment (air, soils, and water) accumulators. The in-plant testing was conducted on a 290-MW cyclone unit burning 110 tons per hour of coal from Kentucky and Southern Illinois. Figure 8 shows the in-plant sample points and Figure 9 diagrams the sample points in the environment. Soil composition was sampled at 1-mile intervals from 20 miles south of the plant to 20 miles north of the plant. The sampling layout was based on atmospheric dispersion modeling calculations using average meteorological conditions for the area and data on particulate emission characteristics. The north-south transect was chosen because of the predominance of north-south winds in the area of the plant. Mud samples were obtained on the bank of the Mississippi River four and fifteen miles north of the plant. These samples would include an effect from discharges to the river upstream of the plant area.

Determinations were made for concentrations of 33 elements for the inplant samples and for 28 elements in the environmental samples. Analytical techniques used for these determinations were neutron activation, isotope-dilution spark-source mass spectrometry, gas chromatography with microwave emission detection, and flameless atomic absorption. Table 23 presents the results of the in-plant chemical analysis of the samples, the mass flow calculations, and the mass balances. The results of the soil sample analysis for the major elements are given in Table 24 and those for the trace elements in Table 25. Table 26 contains the trace element analysis for the water and sediment samples. Results for the determination of mercury content of mosses up to 20 miles north and south of the power plant are given in Table 27.

Table 28 is a comparison of soil analyses from the Allen Steam Plant with the world averages for similar soils. The elements which are concentrated in the plant's flyash over the values for Memphis area soils or similar soils around the world are Se, B, Cu, Ni, Cd, Pb, As, V, Zn, Ga, Ge and Li. If the high concentrations of trace elements in the soil near Allen were due to flyash fallout, a sharp decrease in concentration with depth might be expected. However, there was no appreciable concentration change with soil depth for Cd, Zn, Pb, Cu, As, and V. For the remaining elements the background data for soils was limited.

The authors felt that, although the data were not conclusive, the environmental samples did not indicate any major impact of the Allen Steam Plant emissions on concentrations of trace elements in the surrounding environment.

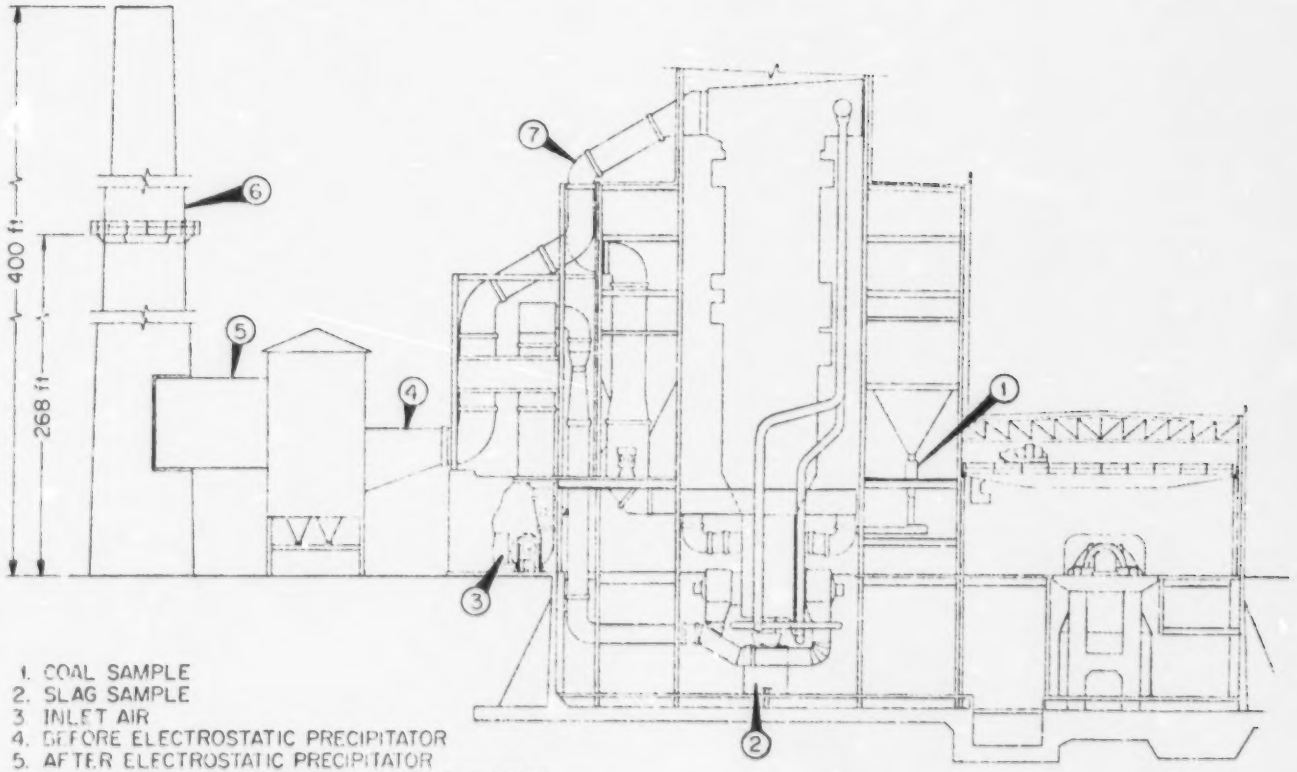
400 ft
268 ft
1. COAL SAMPLE
2. SLAG SAMPLE
3. INLET AIR
4. BEFORE ELECTROSTATIC PRECIPITATOR
5. AFTER ELECTROSTATIC PRECIPITATOR
6. STACK SAMPLE AT 268 ft ABOVE GROUND LEVEL
7. ALTERNATE SAMPLE LOCATION FOR NUMBER 4

Figure 8. Sample points for Allen Steam Plant, unit no. 2 (28)

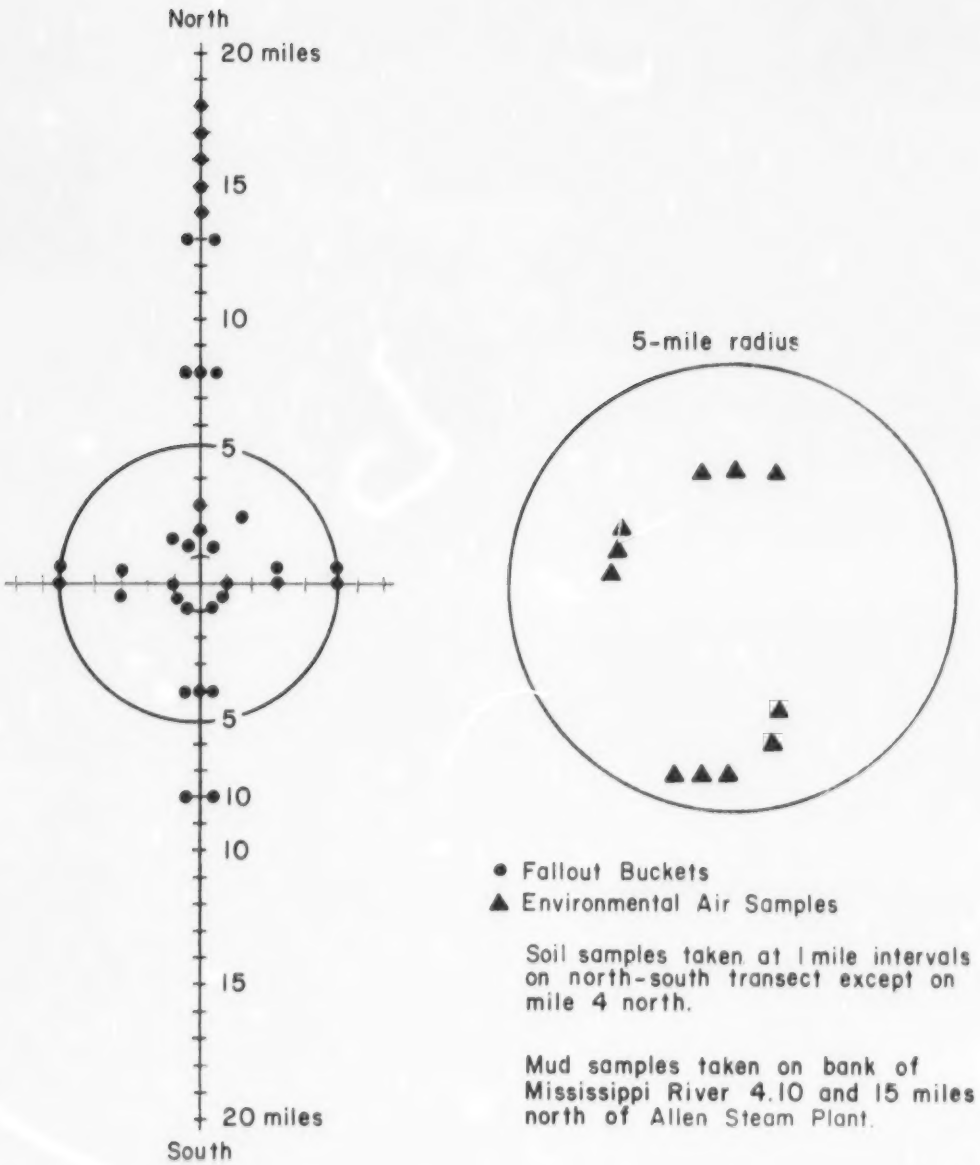

Figure 9. Schematic of sampling locations for soil cores, fallout, and environmental air samples. (28)

TABLE 23. TABULATION OF ELEMENTAL CONCENTRATIONS AND MASS BALANCE RESULTS FROM ALLEN STEAM PLANT (28)

Element	Run	Concentration (ppm unless otherwise indicated)					Mass flow (g/min)					
		Coal	S.T.	P.I.	P.O.	Stack	Coal	S.T.	P.I.	Imbalance (%)[a]	P.O.	Stack
Ag[b]	5	<2	<2	<3–5			<3	<0.20	<0.20–0.33			
	7			<1	~1	1			<0.07		~0.002	0.001
	9	<2–5		<2			<6		<0.10			
Ag[c]	7	<10	<20	10	3	20	<13	<1.0	0.68		0.0056	0.024
Al[b]	5	1.05%	7.6%	5.7%			1.31×10^4	7.5×10^3	3.8×10^3	-14		
	7	1.3%	9.7%	7.4%	20%	38%	1.6×10^4	9.9×10^3	5.0×10^3	-6.9	3.7×10^2	4.5×10^2
	9	1.06%	6.6%	6.9%	3.5%		1.3×10^4	7.2×10^3	3.4×10^3	-18	68	
Al[c]	5	0.9%	5%	5%	20%		1.1×10^4	5.0×10^3	3.3×10^3	-25	3.8×10^2	
	7	>1%	>10%	>10%	>10%	>10%	$>1.3 \times 10^4$	1.0×10^4	$>6.8 \times 10^3$		$>1.9 \times 10^2$	$>1.2 \times 10^2$
	9	1%	5%	15%	10%		1.3×10^4	5.5×10^3	7.3×10^3	-1.5	1.9×10^2	
As[b]	5	4.7	<10	27			5.9	<0.99	1.8			
	7	18		349	138	93	23		24		0.26	0.11
	9	3.8	0.5	46	50		4.7	0.05	2.2	-52	0.097	
As[c]	5	5	1	5	100		6.2	0.10	0.33	-93	0.19	
	7			1000	30	100			68		0.056	0.12
	9	5	2	40	20		6.2	0.22	2.0	-64	0.039	
B[c]	5	200	300	3000	300		250	30	200	-8	0.57	
	7	100	200	250	150	170	130	20	17	-71	0.28	0.20
	9	200	300	2000	300		250	33	97	-48	0.59	
Ba[b]	5	91		400			114		27			
	9	79	600				99	66				
Ba[c]	5	100	300	3000	300		130	30	200	77	0.57	
	7	150	500	300	150	100	190	51	20	-63	0.28	0.12
	9	100	300	1700	100		130	33	83	-11	0.19	
Be[c]	5	<5	5	15	5		<6.3	0.50	1.0		0.01	
	7	0.3	0.5	3	1	0.3	0.4	0.05	0.21	-35	0.0019	0.00036
	9	<5	<10	17	<10		<6.3	<1.1	0.83		<0.019	
Bi[c]	7	<10	<10	2	2	5	<13	<1.0	0.14		0.0037	0.0059
Br[b]	5	2.6	<1	<2–5			3.3	<0.1	<0.13–0.33			
	9	2.0	<0.5	<5	10		2.5	<0.05	<0.24		0.019	

(continued)

TABLE 23. (continued) TABULATION OF ELEMENTAL CONCENTRATIONS AND MASS BALANCE RESULTS FROM ALLEN STEAM PLANT (28)

		Concentration (ppm unless otherwise indicated)					Mass flow (g/min)					
Element	Run	Coal	S.T.	P.I.	P.O.	Stack	Coal	S.T.	P.I.	Imbalance (%)[d]	P.O.	Stack
Ca[b]	5	0.36%	2.06%	1.57%			0.45×10^4	2.0×10^4	1.04×10^4	-32		
	7	0.51%	4.4%	2.2%	1.2%	<1.0%	0.64×10^4	4.5×10^4	1.5×10^4	6.3	22	-12
	9	0.38%	2.7%	1.4%	0.49%		0.47×10^4	3.0×10^4	6.8×10^3	22	9.5	
Ca[c]	5	1%	5%	3.5%	0.3%		1.3×10^4	5.0×10^4	2.3×10^4	-44	5.7	
	7	1%	5%	>1%	<1%	>1%	1.3×10^4	5.1×10^4	$>6.8 \times 10^3$		>19	-12
	9	0.5%	3%	3%	1%		0.6×10^4	3.3×10^4	1.5×10^4	-20	19	
Ce[c]	9	<50					<37					
Cd[c]	5	0.44[d]	2	<2			0.55	0.20	<0.13			
	7			<2	<0.7	<0.7			<0.14		<0.0013	<0.00083
	9	0.50[d]	2	<10–20	7		0.63	0.22	<0.49–0.97		0.014	
Cl[b]	5	407		50			510		3.3			
	9	355		<5–50	1000		460		<0.24–2.4		1.9	
Co[b]	5	3.5	15	35			4.4	1.5	2.3	-14		
	7	5	28	51	26	11	6.3	2.9	3.5	1.6	0.048	0.013
	9	3.3	19	25	58		4.1	2.1	1.2	-19	0.11	
Co[c]	5	10					13					
	7	<10	<50	50	30	10	<13	<5.1	3.4		0.56	0.012
	9	7	40	70	40		9	4.4	3.4	-13	0.078	
Cr[b]	5	23	895				29	89				
	7		111	200				11	14			
	9	21	180	356	300		26	20	17	-32	0.59	
Cr[c]	5	65	300	250	200		81	30	17	-42	0.38	
	7	150	500	170	200	150	190	51	12	-67	0.37	0.18
	9	30	<200	70	40		37	<22	3.4		0.078	
Cs[b]	5	1.5	8.8	15			1.9	0.87	1.0	-1.6		
	9	1.5	8	21	4		1.9	0.88	1.02	0	0.0078	
Cu[c]	5	50	300	300	200		63	30	20	-21	0.38	
	7	100	200	400	400	1000	130	20	27	-64	0.74	1.2
	9	50	200	400	400		63	22	19	-35	0.78	
Dy[c]	9	<10					<13					
Eu[b]	5	0.31	0.7	1.6			0.40	0.07	0.11	-55		
	9	0.17	1.4	1.8			0.21	0.15	0.09	-14		

(continued)

TABLE 23. (continued) TABULATION OF ELEMENTAL CONCENTRATIONS AND MASS BALANCE RESULTS FROM ALLEN STEAM PLANT (28)

Element	Run	Concentration (ppm unless otherwise indicated)					Mass flow (g/min)					
		Coal	S.T.	P.I.	P.O.	Stack	Coal	S.T.	P.I.	Imbalance (%)[a]	P.O.	Stack
Eu[c]	9	~1					~1.3					
Fe[b]	5	1.46%	10.3%	9.5%			1.83×10^4	1.0×10^4	6.3×10^3	-11		
	7	2.0%	13.2%	13.9%	9.6%	4.0%	2.5×10^4	1.4×10^4	9.5×10^3	-6.0	1.8×10^2	4.8×10^1
	9	1.3%	10.1%	9.3%	23.5%		1.6×10^4	1.1×10^4	4.5×10^3	-3.1	4.6×10^2	
Fe[c]	5	2%	10%	10%	10%		2.5×10^4	9.9×10^3	6.6×10^3	-34	1.9×10^2	
	7	~2%	~8%	>2%	>2%	>2%	$\sim 2.5 \times 10^4$	$\sim 8.2 \times 10^3$	$>1.4 \times 10^3$		$>3.7 \times 10^1$	$>2.4 \times 10^1$
	9	2%	10%	10%	10%		2.5×10^4	1.0×10^4	4.9×10^3	-40	1.9×10^2	
Ga[b]	7			71	93	130			4.8		0.17	0.15
Ga[c]	5		40	100	100			4.0	6.6		0.19	
	9	13	<10	70	40		16	<1.1	3.4		0.078	
Ge[c]	5	15	2	200	200		19	0.20	13	-31	0.38	
	9	5	<10	70	40		6.3	<1.1	3.4		0.078	
Hf[b]	5	4.4					5.5					
	9	3.0					3.7					
Hg[c]	5			0.11[d]	<1				0.007[d]		<0.0019	
	9			0.13[d]	~10				0.006[d]		~0.019	
Hg[e]	5	0.064	0.07	0.04			0.080	0.0069	0.0027	-88		
	7	0.170		0.10			0.212		0.007			
	9	0.063	0.09	0.043			0.079	0.0099	0.0021	-85		
K[b]	5	0.20%	1.14%	1.17%			0.25×10^4	1.1×10^3	7.8×10^2	-25		
	7	0.25%	1.46%	1.97%	0.88%	0.29%	0.31×10^4	1.5×10^3	1.3×10^3	-9.7	16	3.5
	9	0.22%	0.95%	1.65%	1.28%		0.27×10^4	1.0×10^3	8.0×10^2	-33	25	
K[c]	5	0.17%	1.5%	1.7%	0.3%		0.21×10^4	1.5×10^3	1.1×10^3	24	5.7	
	7	0.1%	3%	1%	0.5%	0.05%	0.13×10^4	3.1×10^3	6.8×10^2	190	9.3	0.6
	9	0.06%	0.5%	0.7%	0.2%		0.07×10^4	5.5×10^2	3.4×10^2	27	3.9	
La[b]	5	4.8	35	30			6.0	3.5	2.0	-8.3		
	7	6	46	36	19	12	7.5	4.7	2.46	-4.5	0.035	0.014
	9	5.0	42	32			6.3	4.6	1.5	-3.2		
La[c]	9	~10					~13					
Li[c]	5	30	300	350	70		37	30	23	43	0.13	
	7	100	500	200	100	50	130	51	14	-50	0.19	0.059
	9	25	200	300	200		31	22	15	19	0.39	

(continued)

TABLE 23. (continued) TABULATION OF ELEMENTAL CONCENTRATIONS AND MASS BALANCE RESULTS FROM ALLEN STEAM PLANT (28)

Element	Run	Concentration (ppm unless otherwise indicated)					Mass flow (g/min)					
		Coal	S.T.	P.I.	P.O.	Stack	Coal	S.T.	P.I.	Imbalance (%)[a]	P.O.	Stack
Mg[b]	5	0.15%	0.98%	0.89%			0.18×10^4	9.7×10^2	5.9×10^2	-13		
	7	0.17%	1.3%	1.16%		2.5%	0.21×10^4	1.3×10^3	7.9×10^2	-0.4		30
	9	0.17%	0.41%	0.55%	0.88%		0.21×10^4	4.5×10^2	2.7×10^2	66	17	
Mg[c]	5	0.15%	0.6%	1%	0.8%		0.18×10^4	5.9×10^2	6.6×10^2	-31	15	
	7	0.1%	0.5%	>1%	0.7%	1%	0.12×10^4	5.1×10^2	$>6.8 \times 10^2$		13	12
	9	0.15%	0.7%	0.7%	0.4%		0.18×10^4	7.7×10^2	3.4×10^2	-38	7.8	
Mn[b]	5	53	416	325			66	41	22	-4.5		
	7	51	382	316	335	218	64	39	21	-6.3	0.62	0.26
	9	54	418	323	550		67	46	16	-7.5	1.1	
Mn[c]	5	100	1000	1000	1000		130	99	66	27	1.9	
	7	200	700	1000	500	900	250	72	68	-44	0.93	1.1
	9	100	1000	700	500		130	110	34	11	0.97	
Mo[b]	5	47					59					
	9	20					25					
Mo[c]	5	20	100	150	200		25	9.9	10	-20	0.38	
	7	10	70	700	150	70	12	7.2	48	360	0.28	0.083
	9	20	80	200	20		25	8.8	9.7	-26	0.039	
Na[b]	5	0.063–0.63%	0.33%	0.59%			790–7900	3.3×10^3	3.9×10^2			
	7	0.072%	0.29%	0.58%	0.40%	0.33%	900	3.0×10^2	4.0×10^2	-22	7.4	3.9
	9	0.069%	0.32%	0.7%	0.28%		860	3.5×10^2	3.4×10^2	-20	5.5	
Na[c]	5	0.05%	0.3%	0.5%	0.15%		630	3.0×10^2	3.3×10^2	0	2.85	
	7	0.15%	0.3%	>1%	0.3%	0.09%	0.19×10^4	3.1×10^2	$>6.8 \times 10^2$	-48	5.6	1.1
	9	0.03%	0.2%	0.3%	0.2%		370	2.2×10^2	1.5×10^2	0.0	3.9	
Nb[c]	5	<15	2	6	20		<19	0.20	0.40		0.038	
	7	<10	<10	10	10	20	<13	<1.0	0.68		0.019	0.024
	9	~5	2	15	10		~6.3	0.22	0.73		0.019	
Nd[c]	9	~30					~37					
Ni[c]	5	<100	500	500	1000		<130	50	33		1.9	
	7	150	150	1000	500	300	190	15	68	-56	0.93	0.36
	9	<100	500	500	1000		<130	55	24		1.9	
P[c]	5		60	200	200			6.0	13		0.38	
	7			300	300	200			20		0.56	0.24
	9	50	20	500	200		63	2.2	24	-58	0.39	

(continued)

TABLE 23. (continued) TABULATION OF ELEMENTAL CONCENTRATIONS AND MASS BALANCE RESULTS FROM ALLEN STEAM PLANT (28)

Element	Run	Concentration (ppm unless otherwise indicated)					Mass flow (g/min)					
		Coal	S.T.	P.T.	P.O.	Stack	Coal	S.T.	P.T.	Imbalance (%)[a]	P.O.	Stack
Pb[c]	5	<5	3	80	800		<6.3	0.30	5.3		1.5	
	7	~30	<10	300	100	70	~37	<1.0	20		0.19	0.083
	9	<20	3	250	100		<25	0.33	12		0.19	
Pr[c]	9	~10					~13					
Rb[b]	5	17	28	162			21	2.8	11	-34		
	7	20					25					
	9	19.4	100	<120			24.3	11	<5.8			
Rb[c]	5	40	400	650	100		50	40	43	66	0.19	
	7	200		300	50	30	250		20		0.093	0.036
	9	17	40	200	10		21	4.4	9.7	-33	0.019	
S[b]	5	3.5%					4.4×10^4					
	9	5.1%			10.5%		6.4×10^4				2.0×10^2	
Sb[b]	5	<1	<0.2	3.2			<0.75	<0.02	0.2			
Sb[c]	5		8	7	10			0.79	0.47		0.019	
	7			<10	<10	<10			<0.68		<0.019	<0.012
Sc[b]	5	3.4	20	25			4.3	2.0	1.7	-14		
	7	3.6	22	29	10	5	4.5	2.3	2.0	-4.4	0.019	0.0059
	9	3.2	22	25	10		4.0	2.4	1.2	-10	0.019	
Se[b]	5	3.2	9.6	24(<60)			4.0	1.0	1.6(<4.0)			
	7	2.6		23	290	44	3.3		1.6		0.54	0.052
	9	3.2	14	<32–48	760		4.0	1.5	<1.5–2.3		1.4	
Se[c]	9	6	20	20	200		7.5	2.2	0.97	-58	0.39	
Sr[c]	5	5%	30%	30%	30%		6.3×10^4	3.0×10^4	2.0×10^4	-21	5.7×10^2	
	7	5%	>10%	>5%	>5%	>5%	6.3×10^4	$>1.0 \times 10^4$	$>3.4 \times 10^3$		>93	>59
	9	5%	30%	30%	10%		6.3×10^4	3.3×10^4	1.5×10^4	-24	1.9×10^2	
Sm[b]	5	1	0.12				1.3	0.01				
	9	1					1.3					
Sm[c]	9	~10					~13					
Sn[c]	7	20	200	20	20	20	25	20	1.4	-14	0.037	0.024
Sr[c]	7	200	500	300	100	100	250	51	20	-72	0.19	0.12
	9		60	200	60			6.6	9.7		0.12	

(continued)

TABLE 23. (continued) TABULATION OF ELEMENTAL CONCENTRATIONS AND MASS BALANCE RESULTS FROM ALLEN STEAM PLANT (28)

Element	Run	Concentration (ppm unless otherwise indicated)					Mass flow (g/min)					
		Coal	S.T.	P.I.	P.O.	Stack	Coal	S.T.	P.I.	Imbalance (%)[a]	P.O.	Stack
La[b]	5	0.1, 1		1.2			0.13, <1.3		0.08			
	9	<1	2	1.1, <5			<1.3	0.22	0.06, <0.24			
La[c]	7	<10	200	50	20	20	<13	20	3.4		0.037	0.024
Lb[c]	9	~1					~1.3					
Le[c]	5	3	3	<1	<1		3.7	0.30	<0.07		<0.0019	
	9	1	3	~10	~10		1.3	0.33	~0.49		~0.019	
Th[b]	5	2.4		23			3.0		1.5			
	9	3	20	18			3.7	2.2	0.87	17		
Th[c]	7			10	7	3			0.68		0.013	0.0036
Ti[b]	5	580	3300	4200			730	330	280	16		
	7	500	2400	3500	3400		630	250	240	-22	6.3	
	9	710	3000	3700	2500		890	330	180	-43	4.9	
Tl[c]	5	650	3000	~3000	2000		810	300	~200		3.8	
	7	700	3000	1500	700	1000	880	310	100	53	1.3	1.2
	9	700	2000	5000	1000		880	220	240	48	1.9	
Tl[c]	9	<2	2	40	30		<2.5	0.22	1.9		0.059	
	7			100	30				6.8		0.056	
U[b]	5	3	1	15			3.7	0.10	1.0	70		
	7	3.3	17	21	12.4		4.1	1.7	1.4	24	0.023	
	9	1.67	14	17	7		2.09	1.5	0.83	11	0.014	
U[c]	7			100	20	10			6.8		0.037	0.012
V[b]	5	21	135	211			26	13	14	3.8		
	7	69	560	780	406		36	57	53	28	0.75	
	9	21	125	200	63		26	14	9.7	8.8	0.12	
V[c]	5	12	30	100	100		15	3.0	6.6	36	0.19	
	7	50	100	260	100	100	63	10	14	62	0.19	0.12
	9	30	100	350	100		37	11	17	24	0.19	
W[b]	9	<5					<6.3					
W[c]	7	<10		50	20	<5	<13		3.4		0.037	<0.0059
	9	1	1	5	1		1.3	0.11	0.24	73	0.0019	

(continued)

TABLE 23. (continued) TABULATION OF ELEMENTAL CONCENTRATIONS AND MASS BALANCE RESULTS FROM ALLEN STEAM PLANT (28)

Element	Run	Concentration (ppm unless otherwise indicated)					Mass flow (g/min)					
		Coal	S.T.	P.I.	P.O.	Stack	Coal	S.T.	P.I.	Imbalance (%)[a]	P.O.	Stack
Zn[c]	5	250	900	3000	9000		310	89	200	-6.8	17	
	7	<200	<200	500	500	300	<250	<20	34		0.93	0.36
	9	85	100	3000	900		110	11	150	46	1.7	
Zr[c]	5		10	10	100			1.0	0.66		0.19	
	7	40	100	100	50		50	20	6.8	-46	0.093	
	9	<30	10	40	10		<37	1.1	1.9		0.019	

[a] $\text{Imbalance} = \frac{\text{S.T.} + \text{P.I.} - \text{coal}}{\text{coal}} \times 100.$

[b] Neutron activation analysis.

[c] Spark source mass spectroscopy.

[d] Isotope dilution SSMS

[e] Atomic absorption spectroscopy.

ST - Slag tank solids

PI - Precipitator Inlet Flyash

PO - Precipitator Outlet Flyash

(continued)

TABLE 24. MAJOR ELEMENT DATA (PPM, DRY WEIGHT) FOR SOIL SAMPLES COLLECTED FROM A 40-MILE NORTH-SOUTH TRANSECT AT THE ALLEN STEAM PLANT (MEMPHIS, TENNESSEE) (28)

Values represent means of two core samples collected 100 yd apart

Miles North or South	Al	Fe	Mg	Ca	Na	Ti	Mn
N-20		29,300					
N-19	39,760	29,500	8060	2300	8640	2540	547
N-18							
N-17	39,350	35,200	8160	4700	6580	2740	640
N-16		51,700		5000			
N-15		44,900		5000			
N-14		43,300		5000			
N-13	44,750	39,900	8720	3800	5390	3230	797
N-12	40,830	35,600	7940	4100	6990	3040	647
N-11		41,600		4100			
N-10		39,600		3400			
N-9		44,500		4300			
N-8		47,500		5000			
N-7		46,900		5000			
N-6		47,000		4100			
N-5		53,000		4700			
N-4							
N-3	42,710	35,600	8820	3800	6435	3250	387
N-2		29,600		3000			
N-1	37,140	36,000	8040	4000	6920	3150	656
S-1	40,650	30,900	7930	4300	7120	2830	518
S-2	40,430	26,700	7281	2600	9970	2570	375
S-3		32,500		4700			
S-4	34,690	38,500	8060	5000	6750	2710	553
S-5	33,820	39,600	4830	2200	6730	3000	730

TABLE 25. MINOR ELEMENT DATA FOR THE TOP 1 CM OF SOIL COLLECTED FROM A 40-MILE NORTH-SOUTH TRANSECT AT THE ALLEN STEAM PLANT
Values (ppm, dry weight) are means of two core samples collected 100 yd apart at each sampling site (28)

Miles north or south	I-A		II-A	IV-A	V-A		I-B		II-B			III-B		IV-B	V-B		VIII-B	La series	Ac series	
	Rb	Cs	Ba	Pb	As	Sb	Cu	Au	Zn	Cd	Hg	Sc	La	Hf	V	Ta	Co	Eu	Th	U
N-20						1.4	70	0.048			0.028	11.0	41	14.2				1.4	12	3
N-19	118		650	10		1.0	70	0.034		0.5	0.024	11.5	41	12.0	61	0.9	12.6	0.9	10	
N-18		16		10						0.5										
N-17	132		700	18		1.2	83	0.050	360		0.034	14.8	48	12.5	64	0.8	14.5	1.0	13	
N-16	162	41		20		1.7	105		711		0.060	20.2	52	8.0		0.9	19.0	1.1	15	4
N-15	158			100		1.2	97	0.032	425		0.042	18.0	49	9.3		0.8	17.1	1.1	13	
N-14	134	20		75		1.5	90		461		0.067	18.0	48	7.4		0.8	15.7	1.1	14	
N-13	146		640	15	11.5	1.5	87		627	4.0	0.046	17.0	50	13.8	75	1.0	18.0		13	4
N-12	128	17	635	19		1.2	85		537	1.8	0.033	14.0	44	13.0	63	1.0	14.3	1.0	12	4
N-11	138			21		1.0	92		368	0.4	0.034	17.2	49	11.0		1.0	15.4	1.0	13	
N-10	152	24		38		1.1	93	0.055	467	3.5	0.034	17.6	51	9.1		1.0	15.3	1.0	14	4
N-9	156			23		1.4	97		560	4.0	0.035	20.5	54	7.5		1.1	16.0	1.1	15	
N-8	174	64		5		2.0	103		462	1.2	0.047	20.3	51	14.0		0.9	17.0	1.0	14	
N-7	156			5		1.2	94		367		0.038	19.3	47	7.1		0.9	17.5	1.0	14	
N-6	172			11		1.7	106		675		0.043	22.0	55	7.3		1.0	15.3	0.9	13	4
N-5	178			9		1.8	104		423		0.049	20.7	56	6.7		0.8	23.6	1.1	17	
N-4																				
N-3	136			17	10.0	1.5	83		256	1.5	0.045	14.9	48	14.5	70	0.9	16.0	1.0	13	4
N-2	120			16		1.1	78		425	0.9	0.030	11.1	45	12.3		0.8	11.7	1.5	12	4
N-1	130		590	49		1.4	88	0.019	456	0.3	0.044	14.7	48	14.5	60	1.0	15.1	1.0	14	4
S-1	122		715	50		0.9	75	0.033	348	0.3	0.040	13.6	41	12.3	64	0.4	12.8	0.9	12	
S-2	124	17	781	30	7.4	1.2	74	0.036	362	0.4	0.025	11.5	45	14.0	55	1.0	10.5	1.0	11	5
S-3	118			20		1.2	74		416	1.5	0.033	13.6	49	10.0		0.8	13.7	1.0	12	
S-4	138		595	18	7.6	1.4	89		573	1.2	0.043	16.3	53	11.5	58	1.0	14.1	1.1	12	4
S-5	114		494	28		1.4	84		351	0.7	0.029	14.5	47	14.5	52	0.9	13.5	1.2	9	
S-6																				
S-7											0.020									
S-8											0.035									
S-9											0.018									
S-10																				
S-11											0.035									
S-12											0.036									
S-13																				
S-14																				
S-15											0.022									
S-16											0.025									
S-17											0.022									
S-18																				
S-19											0.026									
S-20																				

TABLE 26. MINOR ELEMENT CONCENTRATIONS IN SEDIMENTS AND WATER COLLECTED IN THE IMMEDIATE VICINITY OF THE ALLEN STEAM PLANT IN MEMPHIS, TENNESSEE (28)

Source	Water[a]				Sediments[b]			
	Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn
Steam plant intake (McKeller Lake)	0.008	0.03	0.01	0.28	0.10	3.1	2.5	22.0
Above settling pond outfall (Horn Lake Cutoff)	0.005	0.03	0.02	0.13	1.40	12.0	11.0	51.0
Mouth of settling pond outfall (Horn Lake Cutoff)	0.010	0.04	0.01	0.29	1.40	13.0	11.0	55.0
Below settling pond outfall (Horn Lake Cutoff)	0.011	0.04	0.02	0.40	0.40	12.0	10.0	64.0
Above pumping station (Horn Lake Cutoff)	0.008	0.10	0.11	0.47	0.60	13.0	14.0	59.0
North Horn Lake	0.002	0.03	0.02	0.26	0.20	17.0	14.0	67.0
Cooling water effluent canal	0.009	0.03	0.02	0.17	0.14	4.3	3.3	20.0
Below cooling water effluent outfall (Mississippi River)	0.005	0.02	0.01	0.20				

[a] All water values - ppm.

[b] All sediment values - ppm, dry weight

TABLE 27. MERCURY CONCENTRATIONS (PPM, DRY WEIGHT) IN MOSSES (DICRANUM) EXPRESSED AS A FUNCTION OF DISTANCE NORTH AND SOUTH OF THE ALLEN STEAM PLANT IN MEMPHIS, TENNESSEE (28)

Miles North or South	Hg Concentration (ppm, dry weight)
N-20	
N-18	0.14
N-16	0.43
N-14	0.07
N-12	0.14
N-10	0.25
N-8	0.17
N-6	0.12
N-4	0.32
N-2	0.06
0	
S-2	
S-4	0.46
S-6	0.17
S-8	0.14
S-10	
S-12	
S-14	0.08
S-16	0.11
S-18	0.06
S-20	0.35

TABLE 28. COMPARISON OF ELEMENTAL CONCENTRATIONS IN SOILS COLLECTED IN THE ALLEN STEAM PLANT ENVIRONMENTAL STUDY WITH WORLD AVERAGES (28)

World averages compiled from Vinogradov, Bowen, Goldschmidt and Wedepohl for mineralogically similar soils

Element	Soils in Allen Steam Plant Area		World average (ppm)	Ratio of Allen Steam Plant Average to World Average
	Range (ppm)	Average (ppm)		
Rubidium	114-178	141	100	1.4
Cesium	16-64	28	10	2.8
Barium	494-781	656	500	1.3
Lead	5-100	26	12	2.2
Arsenic	7.4-11.5	9.1	5	1.8
Antimony	0.9-2.0	1.4	~1	1.4
Copper	70-106	88	20	4.4
Gold	0.019-0.055	0.038	<0.1	0.38
Zinc	256-711	458	50	9.2
Cadmium	0.3-4.0	1.4	0.5	2.8
Mercury	0.018-0.067	0.036	0.07	0.51
Scandium	11.0-22.0	15.5	7	2.2
Lanthanum	41-56	48	50	0.96
Hafnium	6.7-14.5	11.2	8	1.4
Vanadium	52-75	62	100	0.62
Tantalum	0.8-1.1	0.9	22	0.04
Cobalt	10.5-23.6	15.4	8	1.9
Europium	0.9-1.5	1.1	1	1.1
Thorium	9-17	13	~6	2.2
Uranium	3-5	4	1	4.0

The results of the study on the in-plant samples were very similar to those of other investigators in that the elements were divided into three classes as follows.

1. Class I - Elements which showed approximately equal concentrations in all phases of the ash sample. This class included Al, Ba, Ca, Ce, Co, Eu, Fe, Hf, K, La, Mg, Mn, Rb, Sc, Si, Sn, Sr, Ta, Th, and Ti.
2. Class II - Elements which showed enrichment in the flyash. This class included As, Cd, Cu, Ga, Pb, Sb, Se, and Zn. These elements were concentrated in the inlet flyash as compared to the bottom ash and in the outlet flyash as compared with the inlet flyash.
3. Class III - Elements which remained essentially completely in the vapor phase. This class included Hg, Cl, and Br.

The other elements analyzed in this study (Cr, Cs, Na, Ni, U, and V) could not be assigned to a specific class based on this data alone. However, they seemed to be intermediate between Class I and Class II.

Canadian Steam Plant[33]

This study consisted of the analysis of 27 monthly coal samples (which were composites of weekly samples from all generating stations) and 5 sets of coal, ash, and flue gas samples collected at one generating station. The samples were analyzed by neutron activation for 33 elements and by existing methods for others (Hg, Cd, Ag, Pb, B, F, and Be). The average concentrations of the elements from the 27 coals and the averages of elements from the coal from the single source were in good agreement.

The conclusions drawn from this study agreed with those previously reported. Certain elements tended to concentrate in different ashes (see Table 4). The authors felt that, of the elements analyzed in this study, only chlorine, mercury, fluorine, and bromine were emitted from the stack in any significant amount. More data is needed for gallium, arsenic, and selenium emissions before any conclusions may be made on the emissions of these elements. The mass balance results for these elements were significantly low on the side of the combustion products.

Three Northern Great Plains Plants[7-10]

This report summarized the trace element emissions from three coal-fired steam-electric generating plants. The unit sampled at Plant "A" was a balanced draft, tangentially-fired, 330-MW boiler with three venturi scrubbers for particulate emission control. This plant used Wyoming sub-bituminous coal at a rate of 141 tons per hour. The unit sampled at Plant "B" was a tangentially fired, 350-MW boiler with a hotside electrostatic precipitator for particulate emission control. The plant also used Wyoming sub-bituminous coal. The coal usage rate at this plant was 138 tons per hour. The unit which was sampled at Plant "C" was a 250-MW cyclone boiler with a mechanical cyclone used as the particulate emission control device.

At each of the plants, all of the incoming and outgoing streams were sampled periodically over a time interval of two days. The flue gas ducts were sampled utilizing a wet electrostatic precipitator sampler. Collection efficiency for this sampler was reported as 99 percent when compared to the EPA filter method. A materials balance approach for 27 elements was used to characterize the effluents around the power plants.

In discussing the results, we note that the amount of an element which exits a steam-electric power plant in each of the various ash streams depends on several factors, including the following.

1. Elemental concentration in the coal.
2. Boiler configuration and firing conditions.
3. Flue gas emission control devices.
4. Properties of the element and its compounds.

As previously mentioned, the first factor depends on the source and type of coal. The latter three factors determine the fractional distribution of the elements among the exiting ash streams.[7]

Ash distribution among exiting ash streams varied with the plants. The tangentially fired boilers at Plants A and B each produced about 22 percent bottom ash, while Plant C's cyclone boiler produced about 63 percent bottom ash. The venturi scrubbers at Plant A and the electrostatic precipitator at Plant B showed collection efficiencies of 99.6 percent and 99.1 percent, respectively. The mechanical collector at Plant C had approximately 65 percent collection efficiency. Thus, Plants A, B, and C had total ash percents in the flue gas of 0.3 percent, 0.7, and 12.9 percent respectively.

This study agreed with other studies discussed in its recognition that elements are partitioned into three distinct groups with respect to their distribution in the ash fractions. Enrichment was noted in the flue gas plus flyash at all three plants for the following elements: S, Hg, Cl, Sb, F, Se, V, Pb, Mo, Ni, B, Zn, Cd, Cr, Cu, Co, U, As, and Ag. Elements which were approximately equally distributed in the bottom ash and flyash included Ba, Be, Fe, Al, Ca, Ti, Mn, and Mg. Some elements enriched in the flue gas (S, Hg, and Cl) were primarily discharged to the atmosphere in the vaporous phase.

The volatilization-condensation theory of enrichment of certain elements in the flyash or stack gas, previously observed by Davison, Natusch, and Wallace, was again noted in this study. This theory holds that some elements or their compounds are volatilized in the fire box of the boiler. Subsequently these vaporous phase elements recondense completely or partially or are discharged through the stack in the gaseous phase. The latter instance is true of sulfur, mercury, and chlorine.

Condensation of elements in the cooler gas streams results in higher concentration of these elements in the fine particulate fractions of flyash, for two reasons.

1. Condensation occurs either by nucleation or by deposition on previously formed particles. Since residence times between volatilization and condensation are relatively low, any nucleation will produce relatively small particles.
2. Deposition occurs on the particle surface and is, therefore, dependent on particle surface area. Since surface area is greater for finer particles, small particulates display increased concentrations of elements which tend to recondense.

The results of the chemical analysis for each of the plants are given in Tables 29, 30, and 31.

Widows Creek Power Plant[29]

This study involved a sampling program around a 125-MW, tangentially fired boiler equipped with a mechanical flyash collector. The purpose of the project was to quantify the potentially hazardous pollutants in the waste streams of a typical, coal-fired utility boiler. In this study 22 trace elements, nitrates, sulfates, polycyclic organic compounds, and polychlorinated biphenyls were identified as potentially hazardous air pollutants resulting from the combustion of coal.

Major findings of this study were as follows:

1. The mass balance for approximately half the elements was closed within acceptable limits of 20 to 25 percent. The causes of the imbalance were inefficient collection of the vaporous metals in the flue gases and analytical errors, particularly in the analysis of coal.
2. An enrichment of the various trace constituents occurred to a moderate degree in the cooler ash streams and to a higher degree in the finer particles of the flyash.

The analytical results for the samples collected are given in Table 32. With the exception of antimony, barium, beryllium, manganese, tellurium, titanium, and vanadium, there was a tendency for potentially hazardous pollutants to progressively concentrate in the ash streams farther downstream from the boiler. Fine particles were enriched with most of the trace metals. Beryllium, cadmium, copper, and zinc exhibited the greatest degree of enrichment in these particles. Another finding was that organic compounds found in the coal, such as polycyclic organic material (POM), were approximately evenly distributed between the bottom ash and the collector ash during one test period. The polychlorinated biphenyls (PCB) were apparently formed during the combustion of the coal. None of these were found in the coal, but they were found in all of the ash streams.

The vaporization-condensation postulate for the enrichment of trace elements in various effluent streams (which has been supported by all of the studies discussed) is further corroborated by comparing the flue gas temperatures at various stages in the combustion process (Figure 10) with the volatility

TABLE 29. ANALYTICAL RESULTS OF THE STATION I SAMPLES[a](8)

Element	Coal	Clear Pond Return	Cooling Tower Blowdown	Lime	Bottom Ash	Bottom Ash Sluice Water	Scrubber Slurry Solids	Scrubber Slurry Liquid	Economizer Ash	Combined WEP
Aluminum	2.3%	5.0	2.2	.30%	10.3%	2.4	10.8%	4.8	10.0%	20.
Antimony	.53	.024	.024	.6	.39	.041	2.3	.036	2.1	.002
Arsenic	.83	.0045	.003	.06	1.3	.0041	5.2	.0013	3.3	.026
Barium	130.	.5	.5	<40.	670.	.5	840.	.5	800.	.5
Beryllium	.82	.0013	.0036	1.2	2.5	.0013	3.2	.0015	3.2	.0014
Boron	51.	3.2	.27	6.8	160.	2.5	220.	2.8	260.	.81
Cadmium	.18	.0034	.001	.46	1.0	.0038	1.8	.0068	7.3	.0095
Calcium	1.76%	790.	140.	53.5	8.66%	790.	11.8%	910.	11.5%	68.
Chlorine	44.	28.	25.	125.	140.	28.	89.	28.	200.	22.
Chromium	21.	.074	.056	12.	67.	.12	118.	.14	.114	.92
Cobalt	2.1	.0081	.026	1.4	7.0	.005	8.1	.011	15.	.016
Copper	34.	.036	.24	17.	93.	.024	155.	.049	105.	.07
Fluorine	140.	20.	.91	520.	100.	16.	820.	20.	120.	1.22
Iron	.40%	.31	1.2	.12%	2.51%	.30	2.25%	.74	2.15%	10.
Lead	4.2	.008	.016	11.	7.1	.007	49.	.023	15.	.061
Manganese	170.	.86	.10	77.	690.	.79	.10%	.88	.10%	.27
Magnesium	.29%	68.	37.	.46%	1.20%	68.	1.36%	62.	1.47%	11.
Mercury	.13	.0005	.0004	.057	.014	.0005	.053	.0007	.010	.004
Molybdenum	4.0	.035	.05	4.5	3.7	.056	10.	.015	34.	.43
Nickel	9.0	.025	.005	3.3	39.	.015	38.	.015	47.	.12
Selenium	2.2	.048	.0037	.27	.70	.031	8.7	.12	.46	.020
Titanium	.11%	.1	.1	87.	.45%	.1	.40%	.1	.48%	.96
Silver	.045	.0003	.0003	.013	.11	.0004	.23	.0005	.093	.0008
Sulfur	.72%	785.	.27%	29.	.11	770.	1.44%	865.	.30	2370
Uranium	1.3	.010	.015	7.8	13.	.0058	3.6	.0087	7.6	.0069
Vanadium	51.	.16	.14	31.	230.	.19	268.	.23	275.	.50
Zinc	24.	.10	.40	6.3	41.	.076	190.	.089	57.	.30

[a] Values represent the average of duplicate determinations. Values for liquid samples are reported as ug/ml and solids samples as ppm on a dry basis, unless otherwise noted. WEP analysis in 10^{-8} lb/scf (60°F, 29.92" Hg).

[b] Analysis from reserve WEP (529).

TABLE 30. ANALYTICAL RESULTS OF THE STATION II SAMPLES[a] (9)

Element	Coal	Inlet Sluice Water	Precipitator Ash	Sluice Ash	Sluice Ash Filtrate	Combined WEP
Aluminum	.71%	<.1	12%	10.9%	9.2	31.
Antimony	.16	.0023	2.3	<.08	.0038	.0029
Arsenic	2.5	<.0001	48.	1.4	<.0001	.0007
Barium	460.	<.6	.78%	.52%	<.6	.26
Beryllium	.29	<.002	5.6	4.1	<.002	.0042
Boron	31.	.17	550.	240.	.49	.92
Cadmium	<.1	<.002	1.2	<.8	<.002	.0016
Calcium	1.09%	57.	19.5%	15.1%	113.	55.
Chlorine	9.4	8.6	47.	<1.	15.	29.
Chromium	9.3	<.053	116.		<.053	.59
Cobalt	1.5	<.003	27.	18.	<.003	.015
Copper	31.	.012	460.	230.	.022	.12
Fluorine	67.	.45	1130.	19.	.70	2.7
Iron	.21%	.12	2.95%	4.06%	.01	9.5
Lead	2.3	.017	22.	11.	.006	.060
Manganese	24.	.034	406.	310.	.016	.18
Magnesium	.15%	15.	2.80%	2.06%	16.	8.1
Mercury	.14	.08	<.010	<.010	<.0004	.017
Molybdenum	.64	<.0002	8.4	3.5	.015	.031
Nickel	2.1	<.02	37.	27.	<.02	.29
Selenium	1.6	.0017	6.8	.35	.0038	.12
Titanium	565.	<.1	.96%	.91%	<.1	2.2
Silver	.048	<.0003	.90	.11	<.0003	.0003
Sulfur	.49%	14.	.80%	910.	108.	2380.
Uranium	.89	.0084	5.8	5.0	.0044	.0031
Vanadium	20.0	0.058	295.	190.	0.071	.26
Zinc	4.1	.39	77.	156.	.0084	.084

[a] Values represent the average of duplicate determinations. Values for liquid samples are reported as µg/ml and solids samples as ppm on a dry basis, unless otherwise noted. WEP values are reported as 10^{-8} lb/scf (60°F, 29.92" Hg).

TABLE 31. ANALYTICAL RESULTS OF THE STATION III SAMPLES [a] (10)

Element	Coal	Ash Sluice Water Inlet	Bottom Ash	Bottom Ash Water Sluice	Economizer Ash	Economizer Ash Sluice Water	Cyclone Ash	South Duct WEP	North Duct WEP
Aluminum	.74%	.42	8.79%	1.7	8.48%	.58	7.44%	730	440
Antimony	.40	.018	.8	.034	.56	.021	.79	.18	.13
Arsenic	8.0	.006	20.	.0087	126.	.0012	188.	.67	1.3
Barium	440.	<.5	.57%	<.5	.83%	<.5	.77%	<5.8	5.3
Beryllium	.60	.0014	5.3	.0017	8.8	.003	8.3	.027	.021
Boron	150.	.26	520.	.25	740.	2.4	.16%	.71	.34
Cadnium	.20	.0003	.87	.0011	1.8	.0012	2.9	.054	.059
Calcium	1.38%	35.	13.0%	43.	12.0%	46.	13.1%	1800	1100
Chlorine	55.	12.	88.	16.	119.	17.	135.	29	43
Chromium	13.	<.053	95.	<.053	121	<.053	86.	3.5	3.6
Cobalt	.75	.0003	10.	.0041	12.	.0039	13.	.28	.21
Copper	10.5	.0084	50.	.014	94.	.008	145.	1.9	1.6
Fluorine	57.	.21	<10.	.25	65.	.21	670.	29	33
Iron	.75%	.43	6.54%	2.1	6.69%	1.4	5.76%	930	550
Lead	.86	.015	<.8	.024	8.3	.025	8.2	.28	.33
Magnesium	.37%	26.	3.71%	26.	3.77%	24.	3.63%	7.1	4.3
Manganese	79.	.082	720.	.055	900.	.096	750.	450	260
Mercury	.074	<.0005	<.010	<.0005	.12	<.0005	.17	.080	.086
Molybdenum	2.0	.033	18.	.016	44.	.012	61.	2.1	3.7
Nickel	5.4	.006	23.	.0014	36.	.007	38.	2.3	3.0
Selenium	1.3	.0012	.25	.0011	.14	.0012	9.5	.31	.26
Titanium	350.	<.1	.35%	<.1	.38%	<.1	.30%	15	18
Silver	.034	<.0003	.11	<.0003	.32	<.0003	.75	<.0031	<.003
Sulfur	1.44%	68.	95.	74.	.13%	77.	.87%	7000	7400
Uranium	1.5	.0022	3.2	.0035	11.	.0044	12.	.15	.086
Vanadium	15.	<.005	140.	<.005	110.	<.005	86.	2.5	2.2
Zinc	7.8	.013	18.	.013	140.	.028	120.	3.5	2.2

[a] Values represent the average of duplicate determinations. Values for liquid samples are reported as ug/ml and solids samples as ppm on a dry basis, unless otherwise noted. WEP values are reported as 10^{-6} lb/sc f (60°F, 29.92" Hg).

TABLE 32. POLLUTANT CONCENTRATION (ppm)[a] IN COAL, ASH, AND FLUE GAS STREAMS AT WIDOWS CREEK STEAM PLANT (29)

Pollutant	Run	Coal	Bottom ash	Superheater ash	Inlet fly ash	Dust collector ash	Outlet fly ash
Trace elements (cations)							
Antimony	2	< 1.3	1.3	0.31	0.55	b/	1.54
	3	0.7	1.4	1.3	< 1.0	1.4	1.36
	4	< 1.2	1.3	1.1	< 1.3	0.32	1.5
	Avg.	< 1.1	1.3	0.90	< 0.95	< 0.9	1.5
Arsenic	2	13.0	5.6	12.1	8.2	b/	7.4
	3	13.5	7.6	3.2	8.1	b/	5.5
	4	16.3	4.2	5.7	8.8	b/	12.0
	Avg.	14.3	5.8	7.0	8.4	b/	8.3
Barium	2	< 167	905	1,119	1,054	1,213	1,028
	3	< 173	844	592	604	916	1,262
	4	< 165	444	715	986	1,367	931
	Avg.	< 168	731	809	881	1,165	1,074
Beryllium	2	1.6	8.0	6.4	8.2	7.2	10.0
	3	1.5	7.4	5.6	7.7	6.8	8.5
	4	1.4	6.5	6.2	8.2	9.7	9.5
	Avg.	1.5	7.3	6.1	8.0	7.9	9 3
Cadmium	2	1.25	0.50	1.46	4.42	2.89	6.29
	3	0.31	2.01	1.35	4.18	1.14	3.88
	4.	1.40	0.74	1.98	10.73	2.00	14.09
	Avg.	0.99	1.08	1.60	6.44	2.01	8.09
Chromium	2	24	125	109	296	133	316
	3	24	132	105	168	191	170
	4	23	116	130	153	128	174
	Avg.	24	124	115	206	151	220

(continued)

TABLE 32. (continued) POLLUTANT CONCENTRATION (ppm)[a] IN COAL, ASH, AND FLUE GAS STREAMS AT WIDOWS CREEK STEAM PLANT (29)

Pollutant	Run	Coal	Bottom ash	Superheater ash	Inlet fly ash	Dust collector ash	Outlet fly ash
Cobalt	2	1.84	5.74	5.86	7.09	10.5	3.61
	3	1.51	1.95	4.45	6.49	6.87	2.78
	4	0.99	3.20	3.93	4.36	6.41	4.68
	Avg.	1.45	3.63	4.75	5.98	7.93	3.69
Copper	2	10	51	54	75	59	81
	3	12	48	46	65	74	70
	4	9	45	45	64	39	72
	Avg.	10	48	48	68	57	74
Lead	2	3.68	6.94	11.9	21.8	21.7	18.7
	3	2.26	12.3	10.4	26.1	11.6	29.9
	4	5.23	5.07	9.41	48.2	11.5	61.2
	Avg.	3.72	8.10	10.6	32.0	14.9	36.6
Manganese	2	24	125	217	153	169	164
	3	30	377	265	222	287	154
	4	51	184	326	371	268	285
	Avg.	35	229	269	249	241	201
Mercury	2	1.88	< 0.541	< 0.58	16.7	< 1.21	23.3
	3	1.91	< 0.489	6.90	23.8	< 1.17	2.2
	4	1.93	< 0.502	46.4	18.3	< 1.17	25.4
	Avg.	1.91	< 0.51	< 18.0	20.0	< 1.18	17.0
Nickel	2	18	45	108	178	88	206
	3	16	84	94	128	98	86
	4	12	58	102	97	60	86
	Avg.	15	62	101	134	82	126

(continued)

TABLE 32 (continued). POLLUTANT CONCENTRATION (ppm)[a] IN COAL, ASH, AND FLUE GAS STREAMS AT WIDOWS CREEK STEAM PLANT (29)

Pollutant	Run	Coal	Bottom ash	Superheater ash	Inlet fly ash	Dust collector ash	Outlet fly ash
Selenium	2	< 6.1	< 5.5	< 6.2	27.9	b/	< 18.9
	3	< 6.1	< 5.9	< 5.7	24.1	b/	< 13.1
	4	6.0	< 5.4	< 5.5	27.5	< 12.5	18.2
	Avg.	< 6.1	< 5.6	< 5.8	26.5	< 12.5	< 16.7
Tellurium	2	< 30	62	30	31	30	< 35
	3	< 30	41	< 27	< 30	31	35
	4	< 30	26	< 27	< 30	28	29
	Avg.	< 30	43	< 28	< 30	30	< 33
Tin	2	1.73	2.83	2.11	3.04	1.74	1.69
	3	1.70	1.81	1.59	3.31	3.48	2.38
	4	1.65	1.45	2.08	2.07	3.45	1.69
	Avg.	1.69	2.03	1.93	2.81	2.89	1.92
Titanium	2	1,090	6,900	5,430	6,420	5,150	6,840
	3	833	5,520	5,480	6,990	6,260	7,410
	4	758	6,010	5,200	5,930	3,940	6,400
	Avg.	895	6,150	5,370	6,450	5,120	6,890
Vanadium	2	61	272	229	308	275	359
	3	61	419	215	238	190	262
	4	64	369	342	478	240	623
	Avg.	62	353	262	341	235	415
Zinc	2	36	68	133	163	154	212
	3	17	275	110	201	131	150
	4	111	107	186	691	164	736
	Avg.	55	150	143	352	150	366

(continued)

TABLE 32 (continued). POLLUTANT CONCENTRATION (ppm)[a] IN COAL, ASH, AND FLUE GAS STREAMS AT WIDOWS CREEK STEAM PLANT (29)

Pollutant	Run	Coal	Bottom ash	Superheater ash	Inlet fly ash	Dust collector ash	Outlet fly ash
Minor elements (cations)							
Calcium	2	11,200	9,500	24,100	9,200	10,500	7,100
	3	11,300	49,300	35,000	18,700	18,900	17,200
	4	13,500	45,500	49,000	40,900	32,200	34,700
	Avg.	12,000	34,800	36,000	22,900	20,500	19,700
Iron	2	19,500	120,000	190,500	95,500	84,600	84,200
	3	23,600	290,400	258,700	156,600	188,700	131,000
	4	26,600	288,400	313,900	172,600	116,500	124,000
	Avg.	23,200	212,900	254,400	142,600	129,900	113,000
Sulfur	2	26,000	900	4,000		11,000	
	3	38,500	2,200	4,200		3,000	
	4	39,500	1,700	4,800		3,950	
	Avg.	34,700	1,600	4,330		5,980	
Anions							
Chloride	2	396	92	27.5	3,400	62	1,335
	3	43	91	37	808	31	125
	4	18	76.5	88	2,260	12	332
	Avg.	152	87	51	2,160	35	597
Fluoride	2	135	9.0	43.0	796	45.5	830
	3	124	10.6	42.8	564	22.5	559
	4	104	12.3	40.7	512	20.6	624
	Avg.	121	10.6	42.2	624	29.5	671
Nitrate	2		15.5	34.0	178	42.1	103
	3		17.7	28.6	307	27.5	88.8
	4		14.7	18.9	57.6	33.2	64.9
	Avg.		16.0	27.2	181	34.3	85.6

(continued)

TABLE 32 (continued). POLLUTANT CONCENTRATION (ppm)[a] IN COAL, ASH, AND FLUE GAS STREAMS AT WIDOWS CREEK STEAM PLANT (29)

Pollutant	Run	Coal	Bottom ash	Superheater ash	Inlet fly ash	Dust collector ash	Outlet fly ash
Sulfate	2		116	7,130	5,570	2,110	3,970
	3		1,090	6,580	7,000	2,520	4,310
	4		818	7,430	8,400	3,510	8,020
	Avg.		675	7,050	6,990	2,710	5,430
Organics[c]							
POM (1)	2	2.5	0.2	ND		0.2	
	3	9.6	ND	ND		0.2	
	4	2.1	ND	ND		0.2	
	Avg.	4.7	< 0.2	ND		0.2	
POM (2)	2	ND	0.2	ND		ND	
	3	ND	ND	ND		ND	
	4	ND	ND	ND		ND	
	Avg.	ND	< 0.2	ND		ND	
POM (3)	2	ND	0.2	ND		ND	
	3	ND	ND	ND		ND	
	4	ND	ND	ND		ND	
	Avg.	ND	< 0.2	ND		ND	
PCB's (all)	2	ND	0.04	0.08		0.16	
	3	ND	ND	0.06		0.04	
	4	ND	0.02	0.12		0.02	
	Avg.	ND	0.02	0.09		0.07	

a/ Parts per million by weight.
b/ No sample left.
c/ POM compounds:
(1) 7,12-Dimethylbenz[a]anthracene
(2) 3,4-Benzopyrene
(3) 3-Methylcholanthrene

Note: ND = None detected.

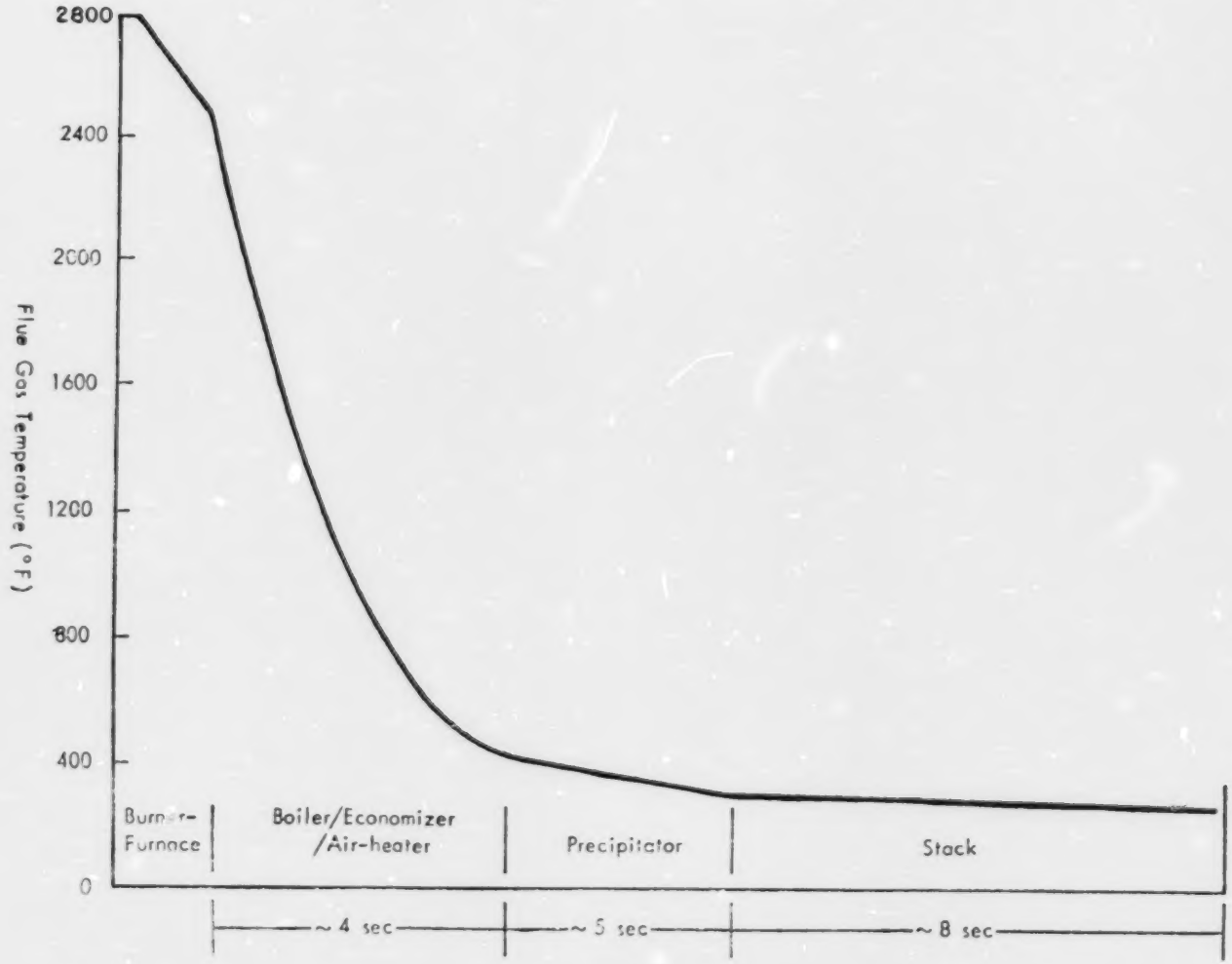

Figure 10. Temperature history of flue gases. (20)

index of the trace elements (Table 33). Usually the more volatile the element, the more likely that it will be emitted from the plant as an uncondensed vapor or as a fine particulate. The only element which failed to follow this postulate is beryllium. According to the Widows Creek report, it was the only potentially hazardous element emitted in the gas stream at a concentration near its threshold limit value.

The reports discussed above concluded that certain elements are enriched in the smaller particles produced by the combustion of coal. These fine, more enriched particles are also the ones most easily passed through particulate control devices. Natusch et al.[4] reported that many of the elements are enriched 100-1000 fold over their natural abundance in the earth's crust. The major portion of this enriched particulate mass occurs in the 0.5-10.0 micron particle diameter range. Particles of this size are commonly inhaled and deposited in the human respiratory system.

Lee and von Lehmden[36] studied trace metal pollution in the environment. Table 34 shows the concentration and the particle size of trace metal particles in urban air. Airborne metals which were measured at concentrations greater than 1 $\mu g/m^3$ included iron, lead, zinc, and magnesium. These elements are all emitted from coal-fired power plants as well as from certain other industrial sources. Also, examination of the trace metals emitted in flyash (see Table 35) shows that some metals, such as cadmium, chromium, manganese, and lead, are more concentrated in the smaller particles emitted. Since these fine particulates are more apt to be inhaled than the larger ones, they may present a greater environmental hazard. Table 36 shows the distribution of flyash sampled at the inlet and outlet of the collector. The outlet flyash contains a much greater proportion of the small particulates than the inlet flyash. Thus, the smaller particles in which trace elements are generally more concentrated are also the ones most easily passed through collectors and the ones which are more respirable. It is the combination of these characteristics which makes fine particulates a source of growing concern.

METHODS FOR CHEMICAL ANALYSIS OF COAL AND FLYASH

Since the above discussions on chemical characteristics of coal and ash include values determined by a variety of analytical methods, a review and comparison of these methods is needed.

Early chemical analyses of coal and its ashes was limited to the major elements (Si, Al, Fe, Ca, S, and Mg). In 1935, Goldschmidt and Peters of the United States Geological Survey (USGS) performed the first trace element analysis of U.S. coal. However, it was not until 1948 that the USGS began an ongoing program for the sampling and analysis of coal for trace elements. The early lack of trace element analysis resulted from the difficulty of applying the classical wet chemistry methods of analysis to trace constituents. However, the advent of newer techniques of instrumental analysis has made analysis of trace elements more feasible. The term trace element is here defined as any element whose concentration is 1000 ppm (0.1 percent) or less.

TABLE 33. VOLATILITY OF TRACE ELEMENTS IN COAL (29)

Volatility Index and Temperature[a,b]				
1	2	3	4	5
< 300°F	300-850°F	850-1300°F		> 1300°F
mercury	selenium	zinc[c]	copper	beryllium
fluorine	arsenic	- - - -	cobalt	boron
thallium	- - - -	barium[c]	lead	titanium
antimony	chlorine		manganese	
	tellurium		nickel[d]	
			chromium[d]	
			cadmium[e]	
			vanadium	
			- - - -	
			tin	

a/ Entries above dashed lines are from Occurrence and Distribution of Potentially Volatile Trace Elements in Coal.

b/ Temperature ranges within which volatilization of an element occurs.

c/ Preferentially concentrated in fine particles of fly ash (pulverized firing).

d/ Concentrated in crust of moderate-sized particles of fly ash (pulverized firing).

e/ Large percentage to bottom ash (pulverized firing).

TABLE 34. CONCENTRATION AND SIZE OF TRACE METAL PARTICLES IN URBAN AIR (36)

Metal	Concentration, $\mu g/m^3$	MMD,[a] µm	Particles <1µm, %
Fe	0.6-1.8	2.35-3.57	12-35
Pb	0.3-3.2	0.2-1.43	59-74
Zn	0.1-1.7	0.58-1.79	14-72
Cu	0.05-0.9	0.87-2.78	16-61
Ni	0.04-0.11	0.83-1.67	28-55
Mn	0.02-0.17	1.34-3.04	13-40
V	0.06-0.86	0.35-1.25	41-72
Cd	0-0.08	1.54-3.1	22-28
Ba	0-0.09	1.95-2.26	20-31
Cr	0.005-0.31	1.5-1.9	45-74
Sn	0-0.09	0.93-1.53	28-55
Mg	0.42-7.21	4.5-7.2	17-23

[a]The mass median diameter (MMD) represents the approximate "average" aerodynamic particle size, i.e., 50% of the particles are above this size and 50% are below.

TABLE 35. TRACE METALS IN FLY ASH AS A FUNCTION OF PARTICLE SIZE (36)

Element[a]	Concentration, ppm				
	25 μm	12.5 μm	10 μm	3.5 μm	1.5 μm
Al	67,000	54,300	57,300	63,600	59,300
B	300	500	500	500	500
Be	2	1	2	2	2
Cd	<5	<5	<5	<5	100
Cr	130	130	130	300	300
Cu	150	150	200	200	200
Fe	40,000	59,000	43,500	35,500	32,300
Mn	200	240	290	390	500
Ni	300	200	200	300	300
Pb	300	200	300	300	500
V	200	200	200	200	200

[a]Sample collected from a coal-fired steam power plant and analyzed by neutron activation and spark source mass spectrometry.

TABLE 36. PERCENT PARTICLE MASS AS FUNCTION OF SIZE [a] (3)

Diameter μ	Sample Set A																		Sample Set B			
	Total Particulate		Fe		V		Cr		Ni		Mn		Pb		Sb		Cd		Zn		Total Particulate		Se [b]	
	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
Above 30	24	5	15	8	6	0	16	0	40	0	0	0	18	0	0	0	12	12	15	2	21	5	7	8
20-30	21	6	6	5	7	0	14	0	4	0	8	0	6	0	0	0	11	8	6	6	19	6	5	6
10-20	38	17	15	9	17	12	26	0	18	13	89	0	20	1	0	0	22	10	21	30	31	18	9	16
5-10	13	20	16	14	20	10	7	0	23	43	33	0	6	9	0	0	15	20	26	10	19	19	19	18
1-5	3	38	30	45	31	43	25	20	7	30	0	0	29	40	0	38	5	30	17	8	7	37	9	22
0-1	1	14	18	19	19	35	12	80	8	14	0	0	21	50	100	62	35	20	15	44	3	15	51	30

[a] Samples collected at the inlet and at the outlet of an electrostatic precipitator control device.

[b] Analysis by neutron activation.

Description of Methods

Instrumental methods often used for the determination of trace elements in coal or flyash include atomic absorption spectrometry, neutron and photon activation analysis, spark-source mass spectrometry, optical emission spectrometry, visible and ultraviolet absorption spectrophotometry, X-ray fluorescence, voltammetry, and potentiometry (ion-selective electrodes), among others.

These methods may be separated generally into two categories. One category includes methods for the determination of more than one element in a single sample. This is especially convenient when large numbers of samples must be analyzed for several elements. Examples of these methods are neutron activation, photon activation, X-ray fluorescence, spark-source mass spectrometry, and optical emission spectroscopy which includes plasma arc emission spectroscopy with multi-element reader.

The second category includes methods which cannot be easily used for multi-element analyses on an individual sample. Therefore, many of these methods may require large quantities of sample if more than a few elements are to be determined. These methods, which include atomic absorption spectroscopy, potentiometry, voltammetry, and absorption spectrophotometry, require sample preparation for the coal and flyash matrices. This sample preparation, usually the wet or dry ashing of coal or the dissolution of flyash through acid treatment or fusion, offers opportunity for sample contamination. However, with the use of appropriate standards and/or the method of standard additions, detection limits can be good. Precision depends largely on the individual analyst's skill. An additional advantage of methods in this category is that the equipment required is comparatively inexpensive.[5]

Let us first consider the methods in this latter group. In atomic absorption spectroscopy (AAS), for example, the sample in solution is atomized by a flame or other energy source, where it produces atomic vapor of the element being analyzed. Monochromatic light which is the same wavelength as that of the required element is then passed through the sample vapor. The atoms present in the ground state (unexcited state) of the vapor absorb radiation from the monochromatic light source in proportion to their concentration present in the sample.[16]

Types of interference encountered in using atomic absorption spectroscopy for coal or ash samples include interelement or chemical interferences, matrix effects (which stem from the large concentrations of acids and solids in solution), and molecular absorptions (which predominately occur from species such as SrO or CaOH and result in a positive error in the absorption measurement).[37]

Natusch et al.[4] determined Pb, Tl, Ni, As, Cd, and Be in flyash by flame atomic absorption and found results in good agreement with those from spark-source mass spectrometry, except for Tl. Selenium was converted to H_2Se and then analyzed, following the method of Schmidt and Royer.[4] Using standard addition calibrations, a precision of $\pm$ 10 percent for all analyses could be obtained.

Flameless atomic absorption spectroscopy (FAAS) achieves better sensitivity for some elements than does atomic absorption spectroscopy. Information on the background concentration for solvent molecular scattering is necessary in addition to separation and preconcentration of the samples.[5] Improved methods for atomic absorption spectroscopy are presently being developed to make possible the use of this technique for mercury, cadmium, selenium, and arsenic. These improvements include larger samples and special vaporization techniques.[16]

Polarography and fluoride-ion selective electrode are other methods which normally require individual samples for analysis of individual elements. Polarography is not used extensively for trace-element analyses in coal or flyash, although its sensitivity for several elements (for example, cadmium) makes it useful for trace analyses after interfering ions are separated. Trace fluoride determinations are commonly made by fluoride-ion selective electrode, an inexpensive and simple application of potentiometry. A detection limit of 10 ppm for fluoride in whole coal was obtained by Ruch et al.[38] Although extensive sample preparation and digestion was required, precision for repeated measurements was good.[5]

Voltammetry is an electrochemical method in which application of a negative voltage is used to plate metal ions acid-extracted from the sample onto an electrode. The electrode potential is then varied linearly in an anodic direction, which produces a sharp current peak proportional to the concentration in the sample.[39]

Many methods in the first-mentioned category, those capable of multiple element analysis on a single sample, have another important advantage as well as the multiple element analysis. Since the organic material in the coal is the major source of interference in many trace element determinations, procedures to reduce or remove this interference through ashing or destruction of the sample are common in many analytical methods. These procedures are expensive, time consuming, and introduce a potentially serious source of error. Some of the newer methods contained in this category, however, do not require ashing or destruction of the sample and, therefore, eliminate this significant source of error.

Instrumental neutron activation analysis (INAA) is one such non-destructive method of analysis. In this method, the sample is irradiated in a nuclear reactor directly, without chemical dissolution or extraction. When bombarded thus with slow neutrons, many elements give rise to radioactive isotopes. When the other components of the sample do not interfere, it is possible to identify the elements present and their concentrations from measurement of intensities of different peaks in the gamma ray spectrum. This method offers high sensitivity and the capability for multi-element determinations. The Oak Ridge National Laboratory study at the Tennessee Valley Authority's Allen Steam Plant reported results by instrumental neutron activation analysis with accuracies of 5 to 10 percent for submicrogram quantities. Gordon reported accuracies of 2 to 3 percent in trace element studies at the Chalk Point Station using this method.[40]

In a recent study, four laboratories measured the concentrations of 37 elements in National Bureau of Standards standard coal samples (SRM 1632) and 41 elements in the standard reference for flyash (SRM 1633), using instrumental neutron activation analysis. Their conclusions were as follows: "In cases where comparisons can be made, both the accuracy and interlaboratory dispersion of results obtained in the analysis of coal and flyash by nuclear methods are generally superior to other methods using in the round-robin study. We suspect that the major reason for this performance of the technique is the fact that virtually no pretreatment of the samples is needed. Thus, we avoid the difficulties encountered in dissolving samples that can occur with the use of other methods such as AAS: loss of volatile species, incomplete dissolution of certain fractions, loss of elements on insoluble residues or container walls, and contamination of samples by impurities in reagents or container materials. Also, because of the long ranges of projectiles and emitted X-rays, the nuclear methods are almost completely free of matrix effects."[11]

For a few elements, the sensitivity of neutron activation can be much improved by radiochemical separations to remove those elements which have interfering radioactivities. Although these separations allow more opportunity for sample contamination, usually limit the analysis to one element per sample, and are slower, it is possible to obtain high precision and accuracy. Radiochemical separations on low-temperature coal ash samples to determine As, Se, Zn, Cd, and Ga were carried out by Ruch et al.[38] However, there are cases in which INAA gives a completely false measurement due to the snythesis of elements in nuclear bombardment. For example, National Bureau of Standards studies on strontium in granite represent one such case.[16]

Instrumental photon activation analysis (IPAA), a nuclear method similar to instrumental neutron activation analysis, is one by which the elements As, Ni, Pb, Sb, Ni, Br, and I can be easily measured in the submicrogram range. A significant drawback to this method, however, is that it requires the bremsstrahlung produced by an electron accelerator for irradiation of the sample.[5]

Spark-source mass spectrometry (SSMS) is another survey method with good sensitivity. In this method the sample, compounded in a silver or graphite electrode, is ionized with a high intensity spark. A determination is then made of the intensities of the ions of different mass-to-charge ratios; they define different radial paths in a magnetic field and, therefore, come to a focus at varying points along a photographic plate positioned on the focal plane of the magnetic analyzer. Other modes of detecting individual isotopes include scanning of the ion species at a collector slit located at the principal focus or use of electric static peak switching with static integration.[41]

The method of spark-source mass spectrometry has several advantages, including high sensitivity, comprehensive element coverage, and linearity. Determinations may be made for many elements at concentrations as low as 1 ppb; also, semi-quantitative determinations as low as 100 ppb for some

elements can be performed by electrical scanning. This technique allows detection of all elements simultaneously during an electrical scan, including interstitial gases, with minimal spectral overlap, matrix effects, or interelement effects. Also, this method exhibits linear response for ionic species of any element with the ion intensity being proportional to the concentration of that element in the sample.[41]

Although detection limits with this method for most elements in coal and flyash are in the parts-per-billion range, accuracy may be only ± 50 percent, varying with the concentration of interferents, as well as with data interpretation. Accuracy may be improved with the use of standards or with the use of stable isotope dilution (SSMS-ID). For elements having stable isotopes, the accuracy of this method is restricted only by the ± percent homogeneity of photographic emulsion on which ion intensity is recorded.[5]

X-ray fluorescence spectroscopy (XRF) involves production of characteristic fluorescence spectra by irradiation of the sample directly with X-rays. For analyzing air pollution particulates, Birks[42,43] cites the following advantages for this method: no sample preparation is required for filter collections; elements of atomic number 11 and greater can be analyzed with fairly uniform detectability; the technique is nondestructive; and several elements can be determined at one time with available commercial equipment at fairly low cost. Although this method does not have the submicrogram sensitivities obtainable by instrumental neutron activation analysis or spark-source mass spectrometry--isotope dilution, its detection limits may be improved by using preconcentration techniques or standard reference materials. For example, precisions of 10 percent or less for microgram quantities of eight trace elements in coal and ash were obtained by Ruch et al., using X-ray fluorescence.[38]

Optical emission spectroscopy involves excitation of the sample in a spark or arc to produce line spectra of the elements present.[39] Use of preconcentration techniques and/or standards is required here to obtain sensitivity similar to that of instrumental neutron activation analysis or spark-source mass spectrometry--isotope dilution. Direct-reading photoelectric spectrophotometers offer both faster analyses for optical emission spectroscopy and somewhat greater precision than does use of photographic plates. Ruch et al.[38] achieved precision of less than 10 percent for nine elements using direct-reading detection and precision of from 9 to 30 percent on the same samples using photographic detection.[5]

The decision on which of the above methods to use for chemical analysis of trace constituents involves consideration by the investigator of several factors, including the following:

1. Performances of the various methods as to accuracy, precision, and detection limits.
2. Cost and time limitations of the methods.
3. Matrix effects of the methods.
4. Sample size requirement.
5. Degree of sophistication and reliability required of instrumentation.

6. Degree of training required for operation of the instrumentation.

The analytical method chosen in a study thus may depend on the individual requirements and resources of the investigation.

Comparisons of Methods

The previous discussions on the various analytical techniques indicate the capabilities and uses of individual methods. However, it is important to realize that data from studies using different methods for analysis are not strictly comparable betause of differences in performance capabilities among these methods. To make the evaluation of results from different studies more feasible, several instigations have been made to compare the analytical performances of several methods on the same samples.

Von Lehmden et al.[39] undertook the comparison of six analytical methods. In this study, nine laboratories were asked to determine the concentration of 28 elements in portions of the same coal and ash samples. The analytical methods employed were neutron activation analysis, atomic absorption, optical spectrometry, anodic stripping voltammetry, spark-source mass spectrometry, and X-ray fluorescence. The determinations from the different laboratories were evaluated to assess the comparability of the various methods as applied to these matrices. Table 37 shows the results for the coal samples, and the ash results are given in Table 38. The following results were obtained from this study. Only definitive concentrations were used for these conclusions (no less-than values were considered).

1. For at least eight trace elements in coal and ash, reported concentrations varied by more than one order of magnitude. For coal, these elements included Mn, Sb, Se, F, Li, Sn, K, and Ba. For ash, these elements were As, V, Zn, Se, Li, Ag, Sn, Na, and Mg.
2. Reported concentrations for three elements (Se, Li, and Sn), varied by more than an order of magnitude in both coal and ash matrices.
3. Agreement was within an order of magnitude in both matrices for only 9 of the 28 elements. These nine were Si, Ca, S, Sr, Fe, Cr, Ni, Be, and B.
4. Standard samples must be prepared and standard methods of analysis must be developed for this material.

In an effort to resolve the analytical problems, the National Bureau of Standards (NBS), in cooperation with the Environmental Protection Agency, prepared Standard Reference Material (SRM) samples for coal (SRM #1632) and ash (SRM #1633). Portions of these samples were sent to 85 laboratories for analysis. "For many of the elements measured, there were surprisingly wide variations of concentrations reported by the participating laboratories far outside the uncertainties usually quoted for the techniques used. For this reason, it is clear that the standards are badly needed so that laboratories can check their procedures for the elements they claim to be able to measure."[11]

TABLE 37. COAL ANALYSIS COMPARISON FOR TRACE ELEMENTS BY LABORATORY AND BY ANALYTICAL METHOD (39)

Laboratory Code	1	3	6	1	3	2	3	4	5	3	3
Analytical Method	SSMS[a]	SSMS[a]	SSMS[a]	OES[b]	OES[b]	NAA[c]	NAA[c]	NAA[c]	NAA[c]	NAA[c]	AAS
Elements analyzed, ppm (by weight)											
Hg	<2.	<2.	<0.10	NA	NA	<0.2	NA	<0.02	0.03	NA	0.051[d]
Be	0.4	NA	0.4	<1.	<0.1	NA	NA	NA	NA	NA	NA
Cd	6.	<1.	0.7	<30.	<10.	NA	<3	<40.	NA	NA	NA
As	2.	2.	0.25	<100.	<30.	<1.	1.4	1.6	NA	<1.	NA
V	10.	NA	7.7	10.	10.	7.0	5.5	7.	NA	6.0	NA
Mn	20.	3.	1.9	10.	20.	7.6	4.8	6.7	NA	5.0	NA
Ni	<40.	4.	6.0	<10.	<20.	NA	NA	<20.	NA	NA	NA
Sb	0.6	NA	0.04	<30.	<10.	0.14	0.2	0.4	NA	NA	NA
Cr	<30.	7.	12.	<10.	<30.	3.4	5.0	4.8	3.	NA	NA
Zn	<100.	5.	6.6	<100.	<50.	NA	NA	<100.	NA	NA	NA
Cu	10.	9.	4.5	10.	10.	NA	NA	<0.4	NA	NA	NA
Pb	<4.	4.	1.8	<30.	<10.	NA	NA	NA	NA	NA	NA
Se	<15.	<8.	0.1	NA	NA	1.0	5.0	2.0	1.5	NA	NA
B	15.	5.	14.	10.	7.	NA	NA	NA	NA	NA	NA
F	<2.	4.	60.	NA	NA	NA	NA	NA	NA	NA	NA
Li	0.3	NA	2.8	<300.	10.	NA	NA	NA	NA	NA	NA
Ag	<2.	NA	<0.1	<1.	<1.	NA	NA	<2.	NA	NA	NA
Sn	3.	NA	0.19	<30.	<10.	NA	NA	NA	NA	NA	NA
Fe	2000.	2000.	1800.	2000.	3000.	2400.	2700.	3140.	NA	8000.	NA
Sr	100.	50.	46.	<30.	NA	160.	NA	120.	NA	80.	NA
Na	600.	100.	660.	300.	500.	800.	870.	840.	NA	800.	NA

(continued)

TABLE 37. COAL ANALYSIS COMPARISON FOR TRACE ELEMENTS BY LABORATORY AND BY ANALYTICAL METHOD (39)

Laboratory Code	1	3	6	1	3	2	3	4	5	3	3
Analytical Method	SSMS[a]	SSMS[a]	SSMS[a]	OES[b]	OES[b]	NAA[c]	NAA[c]	NAA[c]	NAA[c]	NAA[c]	AAS
Elements analyzed, ppm (by weight)											
K	100.	50.	200.	150.	20.	NA	2200.	280	NA	100	NA
Ca	10,000.	10,000.	5,800.	8,000.	10,000.	NA	5500.	7070.	NA	NA	NA
Si	6000.	10,000.	10,000.	3,000.	20,000.	NA	NA	NA	NA	NA	NA
Mg	2000.	700.	2000.	600.	100.	2600.	NA	920.	NA	1000.	NA
Ba	400.	30.	110.	500.	200.	NA	220.	430.	NA	<2.0	NA

a - Analysis on sample direct

b - DC ARC on sample direct

c - Instrumental NAA

d - Dissolution followed by flameless AAS

Analysis code: NAA, neutron activation analysis

SSMS, spark source mass spectrometry

OES, optical emission spectrometry

AAS, atomic absorption spectrometry

NA, no analysis

TABLE 38. FLYASH ANALYSIS COMPARISON FOR TRACE ELEMENTS BY LABORATORY AND BY ANALYTICAL METHOD (39)

Laboratory code	1	1	3	6	1	1	3	3	9	2	3	4	8	1
Analytical method	SSMS[b]	SSMS[b,c]	SSMS[b]	SSMS[b]	OES[d]	OES[c,d]	OES[d]	DRES[e]	DRES[e]	NAA[f]	NAA[f]	NAA[f]	NAA[f]	AAS
Elements Analyzed, ppm[a]														
Hg	1	0.4	2	0.1	1	1	NA	NA	NA	1	18	0.3	NA	0.21
Be	7	1	5	7	5	4	7	NA	3	NA	NA	NA	NA	NA
Cd	3	6	2	2.3	50	100	NA	NA	NA	NA	NA	90	NA	NA
As	40	100	15	2.8	100	200	50	NA	NA	30	70	54	40	NA
V	250	300	200	290	2000	400	200	NA	180	290	247	382	250	300
Mn	300	150	300	170	500	200	500	NA	NA	317	294	369	250	NA
Ni	100	100	100	45	300	50	300	NA	NA	NA	NA	NA	NA	100
Sb	10	40	NA	5.6	50	100	NA	NA	NA	9.2	7	19	NA	NA
Cr	200	100	100	330	500	100	300	NA	80	108	100	130	NA	150
Zn	200	70	1000	330	100	200	200	NA	350	NA	NA	NA	NA	600
Cu	100	150	200	45	300	200	300	NA	NA	NA	NA	33	NA	90
Pb	200	200	100	180	100	200	200	NA	440	NA	NA	NA	NA	95
Ge	10	15	NA	0.77	NA	NA	NA	NA	NA	8.2	40	12	NA	NA
B	500	200	300	190	300	300	500	NA	NA	NA	NA	NA	NA	NA
F	30	10	100 max	60	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Li	20	60	150	190	20	100	300	NA	NA	NA	NA	NA	NA	NA
Ag	1	2	NA	0.04	3	2	1	NA	NA	NA	NA	NA	NA	NA
Sn	6	15	NA	1.9	20	100	NA	NA	NA	NA	NA	NA	NA	NA
Fe	High	High	10%	5.3%	20%	10%	5.0%	10.5%	13%	17.5%	18.3%	18.1%	26%	17.8%
Sr	150	200	200	69	200	200	500	NA	400	520	NA	180	1000	NA
Na	2000	2000	500	6600	3000	4000	3000	1400	NA	2700	2300	2450	3500	2800
K	High	High	1.%	1.7%	2%	2%	0.5%	NA	NA	NA	1.5%	3.1%	2.5%	2.0%
Ca	High	High	4.0%	1.3%	5%	5%	3.0%	3.7%	3.7%	NA	2.2%	3.9%	NA	4.7%
Si	High	High	10%	major	20%	15%	20%	NA	NA	NA	NA	NA	NA	19.5%
Mg	10,000	10,000	5000	44,000	5000	4000	5000	4000	2200	13,700	7000	3000	4000	6000
Ba	200	600	700	110	200	300	500	NA	NA	NA	200	410	400	NA

a ppm by weight, higher concentrations are specified as percent(%). b Analysis on sample direct. c Duplicate sample submitted for SSMS and OES analysis only. d Dc arc on sample direct. e Dissolution followed by RF spark analysis. f Instrumental NAA. Analysis code: NAA, neutron activation analysis; SSMS, spark source mass spectrometry, OES, optical emission spectrometry; DRES, direct reading emission spectrometry; AAS, atomic absorption spectrometry; NA, no analysis.

In a study by Ondov et al.,[11] four participating laboratories measured the concentrations of 37 elements in the NBS standard coal sample and 41 elements in flyash. The analyses were performed by instrumental neutron activation, photon activation and natural radioactivity. The latter method was used by one laboratory to determine K, Th, and U. The results of the measurements from these four laboratories and those from a study by Faulkerson et al.[2] are given in Table 39 for coal and Table 40 for ash. Both the accuracy and interlaboratory dispersion of results for these methods are generally superior to those for the other methods discussed.

While the results of the activation analysis from this study were good, there is still a need to develop standard procedures for the other methods of analysis. To this end, a task group under the D-5 committee of the American Society for Testing and Materials (ASTM) is currently conducting a round-robin analysis of coal and ash. Work has been essentially completed on the development of standardized methods for the analysis of some trace elements (F, Hg, Be, Cr, Cu, Mn, Ni, Pb, V, Zn) and for the major constituents. It is expected that these methods will appear as ASTM standards in 1978.

TABLE 39. ELEMENTAL CONCENTRATIONS IN NBS COAL
(SRM 1632) (μg/g UNLESS % INDICATED) (2,11)

Element	Maryland Concn	Maryland No. of detns	Battelle Concn (6 detns unless noted)	Livermore Concn (5 detns each)	Wash. State Concn	Wash. State # of detns	ORNL	NBS SRM
Na	399±20	(9)	420±30[a]	313±22	424±20	(5)	390	
Mg(%)	0.16±0.02	(5)	0.23±0.07				.248	
Al(%)	1.78±0.18	(6)	1.78±0.08	2.0±0.1			1.90	
Cl	970 ±140	(12)	800±200	760±60	1020±90	(5)	1000	
K(%)	0.27±0.01	(5)	0.28±0.01	0.226±0.008	0.33±0.10	(5)	.29	
Ca(%)	0.41±0.05	(2)	0.284±0.008[b]	0.42±0.07			.44	
	0.47±0.06[c]	(3)						
Sc	3.7±0.1	(6)	3.4±0.3	3.9±0.2	3.9±0.4	(21)	4.5	
Ti	960±100	(3)	1100±200	1100±100	1140±60	(4)	930	800
	890±200[c]	(3)						
V	37±3	(5)	33±4	38±3	37.7±1.2	(4)	40±3	35±3
Cr	19.7±0.8	(5)	19±2	19±1	21±2	(16)	21±2	20.2±0.5
Mn	41±2	(6)	41±6	48±3			46±3	40±3
Fe(%)	0.86±0.06	(6)	0.81±0.07	0.82±0.04	0.87±0.07	(21)	.84	.87 ±0.03
Co	5.6±0.2	(6)	5.2±0.4	6.0±0.3	5.9±0.4	(21)	5.9	6
Ni			16±4		20±4	(10)		
Zn	30±10	(4)					34	37±4
As	5.7±0.2	(7)	5.7±0.5	5.0±0.7	8.0±0.4	(5)	5.5	5.9±0.6
	8 ±2[c]	(3)						
Se	3.1±0.3	(5)	3.3±0.4	3.5±0.4	3.7±0.4	(11)	3.05	2.9±0.3
Br	20±4	(5)	17±2	19±2	21.4±0.7	(5)	14.2	
Rb	20±2[c]	(3)	19±2		23±2	(11)	19.5	
Sr			170±20		152±21	(21)		
Ag			0.06±0.03					
In				0.20±0.12			.07	
Sb	4.3±3.0	(6)	3.7±2.0	4.1±5.3	3.3±1.1	(15)	4.45	
Cs	1.4±0.1	(5)	1.4±0.1		1.49 ±0.12	(11)	1.4	
Ba	330±20	(6)	390±20	327±19	360±35	(14)	405	
La	11.3±0.5	(5)	10.5±0.5	9.1±0.6	11.9±0.5	(5)	10.5	
Ce	20.4±0.8	(6)		18.5±0.7			18.5	
Sm	1.83±0.07	(13)	1.7±0.3	1.48±0.07				
Eu	0.38±0.03	(6)	0.28±0.01	0.32±0.01	0.33±0.04	(10)	0.21	
Tb	0.22±0.05	(5)	0.23±0.06					
Yb	0.7±0.1	(5)						
Lu	0.14±0.01	(6)						
Hf	0.95±0.05	(5)	0.97±0.1	0.72±0.06	0.97±0.10	(21)	.95	
Ta	0.21±0.02	(7)	0.23±0.05		0.29±0.05	(21)	.17	
W	0.87±0.10	(5)		0.6 ±0.3				
Th	3.0±0.2	(6)	3.4±0.6	3.0±0.2	3.1±0.2	(16)	3.0	3.0
			3.45±0.10[b,d]					
U			1.41±0.07[b,d]				1.26	

a Twelve determinations. b Determined by direct X-ray counting of natural radioactivity. c Determined by instrumental photon activation analysis. d One sample of 100 g was counted five times for 1000 min each.

TABLE 40. ELEMENTAL CONCENTRATIONS IN NBS FLYASH (SRM 1633) (μg/g UNLESS % INDICATED) (2,11)

Element	Maryland Concn	Maryland No. of detns	Battelle Concn (6 detns unless noted)	Livermore Concn (5 detns each)	Wash. State Concn	Wash. State # of detns	ORNL Concn	NBS Concn
Na	3400 ± 200	(9)	3700 ± 200	2800 ± 200	2970 ± 50	(4)		3070
Mg (%)	1.5 ± 0.16	(6)	2.08 ± 0.43					1.98
Al (%)	13.2 ± 0.5	(5)	12.6 ± 0.4	12.3 ± 0.6			12.5	
Si (%)	21 ± 2[a]	(3)						
Cl	42 ± 10	(4)						
K (%)	1.60 ± 0.08	(5)	1.71 ± 0.03[b]	1.4 ± 0.1	1.73 ± 0.08	(4)	1.8	
Ca (%)	4.2 ± 0.4	(3)		4.5 ± 0.3			4.34	
	5.3 ± 0.5[a]	(3)						
Sc	27 ± 1	(7)	27 ± 1	28 ± 2	26.2 ± 1.7	(20)	32	
Ti	7300 ± 400	(3)	7600 ± 800	7200 ± 700	7550 ± 250	(4)	6420	
	7300 ± 400[a]	(3)						
V	251 ± 26	(6)	220 ± 15	244 ± 24	224 ± 12	(5)	240	214.8
Cr	130 ± 6	(7)	131 ± 8	126 ± 10	122 ± 7	(20)	138	131 ± 2
Mn	509 ± 20	(8)	489 ± 11	506 ± 23	480 ± 12	(5)	460	493 ± 7
Fe (%)	6.2 ± 0.3	(7)	6.5 ± 0.3	5.8 ± 0.3	6.2 ± 0.5	(19)	637	
Co	41.2 ± 1.6	(6)	40 ± 2	42 ± 2	42.8 ± 2.1	(14)	46	38
Ni	92 ± 6[a]	(2)			105 ± 13	(10)	109	98 ± 3
Zn	216 ± 25[a]	(3)					208	210 ± 20
As	60 ± 2.5	(9)	61 ± 5	52 ± 3	56 ± 3	(4)	54	61 ± 6
	61.5 ± 3.0[a]	(5)						
Se	10.3 ± 1.4	(5)	8.8 ± 1.2	11.5 ± 1.4				9.4 ± 0.5
Br			12 ± 4					
Rb	126 ± 10[a]	(2)	124 ± 10		126 ± 9	(15)	120	112
Sr			1900 ± 200		1500 ± 200	(20)		
Y	62 ± 10[a]	(3)						
Zr	301 ± 20[a]	(2)						
In				0.32 ± 0.10				
Sb	7.8 ± 0.7	(9)	7.2 ± 0.8	6.4 ± 0.4	6.3 ± 0.4	(10)	7.8	
	7.0 ± 1.1[a]	(3)						
I	2.9 ± 1.2[a]							
Cs	7.9 ± 0.9	(5)	9.9 ± 0.8		8.0 ± 0.8	(11)		
Ba	2700 ± 200	(7)	3400 ± 400	2600 ± 200	2700 ± 50	(20)	2780	
La	82 ± 3	(6)	82 ± 4[c]	65 ± 7	82 ± 2	(4)	82	
Ce	156 ± 12	(8)		135 ± 7				
Sm	13.8 ± 0.6	(8)	12.4 ± 0.5[c]	11.1 ± 0.7			15	
Eu	2.9 ± 0.2	(7)	2.3 ± 0.1	2.2 ± 0.2	2.7 ± 0.2	(15)	2.86	
Tb	1.7 ± 0.25	(5)	2.0 ± 0.3					
Yb	5.1 ± 0.8	(5)	8.9 ± 0.9					
Lu	1.0 ± 0.1	(8)						
Hf	7.9 ± 0.4	(7)	8.2 ± 0.8	5.8 ± 0.9	7.5 ± 0.5	(19)	10.8	
Ta	1.64 ± 0.13	(6)	1.7 ± 0.3		2.1 ± 0.3	(18)	1.6	
W	5.7 ± 1.0	(5)		3.5 ± 1.1				
Pb	75 ± 5[a]	(2)					78 ± 4	70 ± 4
Th	23.5 ± 1.0	(6)	28 ± 2	23 ± 1	23.2 ± 1.6	(19)	26	24
			26.2 ± 1.3[b,d]					
U			12.0 ± 0.5[b,d]				11.8	11.6 ± 0.2

a - Done by instrumental photon activation analysis
b - Done by direct gamma-ray counting of natural radioactivity
c - Twelve determinations
d - One sample of 100 g counted five times for 1,000 min. each

SECTION 8

MODIFIED ASH

The recent establishment of more stringent air pollution regulations for the utility industry may result in significant changes in types of coal ash produced. Changes in present utility practice have been proposed, such as flue gas desulfurization processes, coal gasification and liquefaction processes, greater utilization of certain types of coal, and new power plant designs. While coal fractionation processes would produce residues at the conversion facility, the other three proposals would result in modified residues at the generating plant itself.[12]

Effects of these three proposals have been studied in varying depth. Ashes from different coal types have been summarized above. New power plant designs for reduced environmental impact are largely in the conceptual stages at present. However, several flue gas desulfurization processes have been developed and tested in recent years. These may considerably alter the nature of collected residue. Also, these scrubbing processes generally produce a significantly increased quantity of utility waste residue.[12]

The chemistry of scrubbing power plant stack gases is complex and is still under study. Hollinden[44] explains that "The overall reaction is that of SO_2 with CaO or $CaCO_3$ to form calcium sulfite, with some oxidation of the sulfite to sulfate. The actual reaction path to these end products, however, appears to be complex, with gas-liquid reactions, both ionic and nonionic reactions in the liquid phase and liquid-solid reactions all taking place."

The sludge resulting from the scrubbing of stack gases utilizing lime or limestone has been characterized by Selmeczi and Knight.[45] This sludge contains the same basic elements as those found in bottom ash and flyash (see Table 41). However, the levels of concentrations of most of these elements are generally lower in scrubber sludge due to the dilution effect of the scrubbing slurry and of the SO_2 removed from the gas stream. The chemical composition of the sludge solids is affected by the type of fuel, boiler operating conditions, type of scrubber, liquid-to-gas ratio, pH, chemical composition, and quantity of scrubbing solution used. The chemistry and the quantity of the flyash constituent in the sludge depends on the type of coal burned and the efficiency of any flyash removal system which may be located upstream from the scrubber.[45]

X-ray diffraction studies conducted under the same program gave the following results. "In the conventional lime scrubbing process sludges, the major

TABLE 41. CHEMICAL COMPOSITION OF LIME PROCESS SCRUBBER SLUDGE ON DRY SOLID BASIS (45)
(percent)

Element	Sample A	Sample B	Sample C
SiO_2	31.6	4.9	.58
Al_2O_3	18.3	3.4	1.21
Fe_2O_3	4.3	.6	.39
CaO	18.1	43.2	43.4
MgO	2.4	.2	.01
Total Sulphur	7.2	18.9	20.0
SO_2	12.1	33.0	29.2
SO_3	2.9	5.9	13.6
CO_2	3.2	6.7	7.1
Free Carbon	ND	ND	2.8
Na_2O	ND	ND	.35
K_2O	ND	ND	.03

ND - Not determined

Sample A - Eastern Power Plant - 19% ash; 1.9% sulfur sample taken upstream of flyash collection device.

Sample B - Same as "A" except sludge from scrubber located downstream of flyash collector.

Sample C - Western Power Plant - Scrubber located downstream of ash collector.

component beside flyash is calcium sulfite hemihydrate, $CaSO_3 \cdot 1/2\ H_2O$. Calcium carbonate was not definitely identified, partly because of the low concentration and partly because it was a very poorly crystallized precipitate. Gypsum again was typically missing from the patterns, but a sulfate-containing phase, ettringite, $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot X\ H_2O$, was indicated in the flyash-containing sludges. In the dry-limestone-injected wet scrubbed sludge, gypsum was a major phase, in excess of 5 percent."[45] Both $CaCO_3$ and $CaSO_3 \cdot 1/2\ H_2O$ were identified as major phases in the limestone process sludge.

The crystal morphology of these sludges was also determined by scanning electron microphotographs. These photographs revealed the characteristics of calcium sulfite crystal clusters. Individual crystals were very thin platelets with 10 to 100 micron lateral dimensions and thickness of 0.1 to 0.5 micron. However, since calcium sulfite has a tendency to grow in clusters, single crystals were rarely seen. Depending on the SO_2 content of the gas, the density of a cluster varied considerably. A low-sulfur, western-coal, scrubber sludge was found to have the loosest clusters with increased amounts of gypsum crystals present. Gypsum crystals were not usually observed in sludges produced by wet lime scrubbing of eastern high-sulfur coals. Calcium carbonate was readily identifiable in block forms in the wet limestone scrubbing sludge.[45]

Rossoff and Rossi[46] and Leo and Rossoff[47] of the Aerospace Corporation have also reported on the chemical and physical characteristics of sludges. Seven utility power plants (Table 42), covering a variety of scrubber types, capacities, coal sources, and absorbents were included in the latter report. In addition to sludge characterization, changes in the system chemistry caused by variables such as time, traversal through the system, and pH and ionic strength were also investigated. The following conclusions were derived from their studies.[47]

1. Other than increased concentrations of potassium, which may be due to leaching of flyash, the concentrations of major, minor, and trace elements in scrubber liquors tend generally to decrease along the path of the process.
2. Based on sampling at four of the plants over periods of 4 to 16 months, indications are that a rapid increase in the concentrations of major species occurs and attains comparatively stable conditions at a concentration where the rate at which a constituent is lost in the waste product equals the rate at which that constituent is scrubbed from the flue gas. Trace elements displayed initial increases in concentration following startup. Thereafter, however, except for lead, they did not show a trend in concentration level with time.
3. It appears that trace element concentration of scrubber liquors in a system is not controlled by ionic strength of the liquor or by system pH.
4. In comparing trace metal concentrations in scrubber liquor from the lime, limestone, and double alkali processes, these concentrations (As, Be, Cd, Cr, Cu, Hg, Pb, Se, and Zn) were generally highest in

TABLE 42. FGD SYSTEMS SAMPLED AS DATA BASE (47)

Power Plant	Scrubber System	Scrubbing Capacity, MW (equiv)	Coal Source	Absorbent
TVA Shawnee Steam Plant	Venturi and spray tower, prototype	10	Eastern	Lime
TVA Shawnee Steam Plant	Turbulent contact absorber, prototype	10	Eastern	Limestone
Arizona Public Service Company, Cholla Power Plant	Flooded-disk scrubber, wetted film absorber	120	Western	Limestone, fly ash
Duquesne Light Company, Phillips Power Station	Single- and dual-stage venturi	410	Eastern	Lime
General Motors Corporation, Chevrolet-Parma Power Plant	Bubble-cap tower	32	Eastern	Soda ash, lime
Southern California Edison, Mohave Generating Station	Turbulent contact absorber, pilot plant	< 1	Western	Limestone
Utah Power and Light Company, Gadsby Station	Venturi, and mobile bed, pilot plant	< 1	Western	Soda ash, lime

the limestone system and lowest in the double-alkali system with trace metal concentrations in the lime system falling between the two.

Leo and Rossoff further concluded from their studies that trace element concentrations in the scrubber waste solids and liquors seemed to depend on the trace element concentrations of input materials, especially coal. Variations in the data may be caused by varying quantities of fly ash in the scrubber wastes, as well as the scrubbing efficiency relative to each element. Results of this study indicate that the main source of trace metals in the waste is the fly ash in the waste. Wastes with higher flyash content tend to have higher trace element concentrations. Mercury and selenium are two exceptions. Although they are found at relatively low concentrations in the flyash, existing primarily in the flue gas stream as vapors or very fine particulates, their relative concentrations in scrubber waste are comparable to the other trace elements. This indicates that these elements are at least partially removed from the flue gas.[47]

Table 43 shows the phase composition of the major solid constituents of the sludges in the Aerospace study.[47] The four main crystalline phases contained in these sludges were flyash, calcium sulfite, calcium sulfate, and unreacted limestone or precipitated calcium carbonate. The quantities of these crystalline phases relative to each other depend on factors such as sulfur content of the coal, efficiency of scrubbing SO_2, flyash removal efficiency of the system, stoichiometric ratio of reactants relative to fuel sulfur content, reactant utilization efficiency, and the degree of oxidation of sulfur products in the system.

Scrubber wastes contain fine particulates suspended in an aqueous medium. Particle size for both sulfate and sulfite particles ranges between 1 μm and 100 um, a range comparable to that of flyash particles. However, particle shapes differ; flyash particles are generally spherical, while sulfate particles are block-like and sulfites are plate-like. The thixotropic nature of flue gas desulfurization waste is usually attributed to the plate-like shape of the sulfites.[47]

Viscosity measurements on the seven sludges tested showed that the pumpable mixtures (<20 poise) had solids contents ranging from 32 to 70 percent. Results of the tests suggested that flyash tends to reduce the viscosity of these wastes.[47]

Tables 44 shows the wet bulk densities of eight sludges, each of which was dewatered in the laboratory by four techniques. Results indicate that for most of these sludges, highest density was noted from dewatering by vacuum-assisted filtration. For the other sludges, centrifugation gave highest density. Sludges with the coarsest particle size distributions showed the best overall dewatering characteristics.[47]

Table 45 gives permeability coefficients for untreated and chemically fixed sludges. For untreated wastes, these generally range from 2×10^{-4} to 1×10^{-5} cm/sec. Chemical treatments tended to result in decreased permeability,

TABLE 43. PHASE COMPOSITION OF FGD WASTE SOLIDS IN WEIGHT PERCENT[a] (47)

Atomic Formula	TVA Shawnee Limestone, 2/1/73	TVA Shawnee Limestone, 7/12/73	TVA Shawnee Limestone, 6/15/74	TVA Shawnee Lime, 3/19/74	SCE Mohave Limestone, 3/30/73	GM Parma Double Alkali, 7/17/74	APS Cholla Limestone, 4/1/74	DLC Phillips Lime, 6/17/74	UPL Gadsby Double Alkali, 8/9/74
$CaSO_4 \cdot 2H_2O$	21.9	15.4	31.2	6.3	84.6	48.3	17.3	19.0	63.8
$CaSO_3 \cdot 1/2H_2O$	18.5	21.4	21.8	48.8	8.0	12.9	10.8	12.9	0.2
$CaSO_4 \cdot 1/2H_2O$						19.2			
$CaCO_3$	38.7	20.2	4.5	2.5	6.3	7.7	2.5	0.2	10.8
$MgSO_4 \cdot 6H_2O$	4.6	3.7	1.9	1.9					
$CaS_2O_3 \cdot 6H_2O$[a]							14.3		
$Na_2SO_4 \cdot 7H_2O$						6.9			
NaCl					1.5				
$CaSO_4$[a]									17.7
CaS_3O_{10}[a]								9.8	
Fly Ash	20.1	40.9	40.1	40.5	3.0	7.4	58.7	59.7	8.6
Total	103.8	101.6	99.5	100.0	103.4	101.4	103.6	101.3	101.1

[a]Phases not explicitly measured; presence deduced from x-ray study.

TABLE 44. DEWATERED BULK DENSITIES OF FGD WASTES (47)

Sample Source and Date	Dewatering Method							
	Settled		Settled and Drained		Centrifuge		Filter	
	Percent Solids	Density, g/cc	Percent Solids	Density, g/cc	Percent Solids	Density, g/cc	Percent Solids	Density, g/cc
Shawnee Limestone, 2/1/73	49.0	1.45	55.7	1.51	59.8	1.56	65.0	1.65
Shawnee Limestone, 6/15/74	52.9	1.46	58.3	1.53	63.3	1.60	65.9	1.64
Shawnee Lime, 3/19/74	41.5	1.34	43.4	1.36	49.9	1.44	56.0	1.51
GM Double Alkali, 7/18/74	40.0	1.31	43.9	1.35	50.9	1.43	57.8	1.52
Utah Double Alkali, 8/9/74	37.2	1.30	41.4	1.33	62.2	1.62	54.6	1.50
Duquesne Lime, 6/17/74	47.6	1.40	53.1	1.48	57.2	1.52	57.0	1.52
Cholla Limestone, 9/1/74	46.7	1.39	50.9	1.44	60.9	1.58	53.4	1.48
Mohave Limestone, 3/30/73	66.6	1.65	67.2	1.67	77.0	1.86	80.3	1.78

TABLE 45. PERMEABILITY OF UNTREATED AND CHEMICALLY FIXED FGC WASTES (47)

Sample Source	Sample Date	Replications[a]	Fractional Void Volume	Permeability Coefficient, cm/sec	Remarks
Shawnee Limestone	2/1/73	1	0.69	2.3×10^{-4}	Column packed as slurry
	6/15/74	3	0.60	1.0×10^{-4}	
	6/15/74	1	0.58	9.6×10^{-5}	
	6/15/74	3	0.58	8.5×10^{-5}	
	6/15/74	3	0.55	5.9×10^{-5}	Compacted wet
Shawnee Lime	3/19/74	1	0.75	1.7×10^{-4}	
	3/19/74	1	0.74	5.3×10^{-5}	Compacted wet
	3/19/74	(2)	0.72	6.0×10^{-5}	
Mohave	3/30/73	(3)	0.47	5.0×10^{-4}	Column packed as slurry
	3/30/73	3	0.43	7.5×10^{-4}	
	3/30/73	3	0.34	1.6×10^{-4}	
Dusquesne	6/17/74	(2)	0.68	1.2×15^{-4}	
	6/17/74	3	0.58	1.3×10^{-4}	
	6/17/74	2	0.49	7.4×10^{-5}	
GM Double Alkali	7/18/74	(2)	0.71	8.2×10^{-5}	
	7/18/74	1	0.69	2.5×10^{-4}	
	7/18/74	1	0.65	8.1×10^{-5}	Compacted wet
Cholla	4/1/74	(2)	0.56	2.7×10^{-5}	
	4/1/74	1	0.54	1.8×10^{-5}	
	4/1/74	1	0.54	1.1×10^{-5}	Compacted wet
Utah Double Alkali	8/9/74	1	0.75	9.8×10^{-4}	
	8/9/74	1	0.73	1.3×10^{-4}	Compacted wet
	8/9/74	(2)	0.70	1.2×10^{-4}	
Shawnee Limestone (IUCS)		(2)	0.69	2.2×10^{-4}	Pulverized
Shawnee Limestone (IUCS)		(5)	0.54	5.5×10^{-8}	Solid, undisturbed
Mohave (IUCS)		(2)	0.55	7.9×10^{-5}	Pulverized
		1	0.65	7.3×10^{-4}	Pulverized
		1	0.53	1.9×10^{-4}	Pulverized, compacted wet
Shawnee Lime (IUCS)	5/29/75	1	0.57	5.5×10^{-5}	Solid, undisturbed
	6/12/75	1	-	5.5×10^{-7}	Solid, undisturbed
Shawnee Limestone (Chemfix)		(2)	0.68	4.1×10^{-5}	Pulverized
		1	0.72	$1.5\text{-}2.1 \times 10^{-5}$	Solid, undisturbed
	2/27/75	1	0.70	4.7×10^{-5}	Pulverized
Shawnee (Dravo)		1	0.78	3.2×10^{-4}	Pulverized
	6/12/75	1	0.75	6.9×10^{-5}	Solid, undisturbed
Duquesne (Calcilox)		(2)	0.70	3.8×10^{-4}	Pulverized
		1	0.78	4.9×10^{-4}	Pulverized
		1	0.76	2.1×10^{-4}	Pulverized, compacted wet

[a]Replications of those in parenthesis refer to multiple measurements on a single column using varying hydraulic heads.

while fracturing the treated wastes increased permeability. Weathering (exposure to the cycle of freezing and thawing) tended to cause cracks in treated wastes in the field and, therefore, to increase permeability.[47]

Compaction of the sludges under load ranged from 5 to 15 percent. Permanent compaction after load release, however, was only 1 to 3 percent.[47] It appears that effective packing occurs only when the sludge involved contains predominantly block-like (gypsum crystals) rather than plate-like particles (sulfite crystals), although it has been seen that the size of the plates can have a dramatic effect on compaction. Large sulfite platelets have been found to settle and compact almost as well as gypsum.[48]

Sludges with solids content of 55 to 70 percent were measured for load bearing strength. A strength of 2.1 to 2.4 x 10^6 dyne/cm^2 was noted for a Shawnee sludge having 70 percent solids. At 55 percent solids, sludges showed virtually no ability to bear load.[47]

Combustion Engineering conducted a study in sludge characterization using a group of 10 samples selected to represent the material that would be produced by various kinds of air pollution control systems using lime or limestone scrubbing (Table 46). The chemical composition of these samples is shown in Table 47.[49,50]

The Dravo Corporation also investigated sludges from various scrubbing systems.[50] The sludges studied were the following.

A. Sludge A was from a power station burning coal with 19 percent ash and 1.9 percent sulfur and using a two-stage venturi lime scrubber. The flue gas for the scrubber was taken upstream from the flyash collecting devices.
B. Sludge B was from the same station, but the gas was scrubbed downstream of the flyash precipitator. This sludge has a lower flyash content.
C. Sludge C was taken from the Chemico installation at the Mitsui Aluminum Company in Ohmuta City, Japan. They were burning a 9,000-Btu brown coal with 30 percent ash and 1.9 percent sulfur and scrubbing with a byproduct of carbide lime. The flyash content of the sludge was estimated to be 5 percent.
D. Sludge D was from a western power plant using a proprietary scrubbing device. Scrubbing occurred downstream from the flyash precipitator and the SO_2 content of the gases was approximately 380 ppm.
E. Sludge E was from a pilot plant based on the dry injection of limestone followed by wet scrubbing (marble bed).
F. Sludge F was obtained from a pilot plant scrubber on a molybdenum sulfide roaster using a four-tray TCA scrubber. The flue gas normally contains 1.2 percent SO_2 and .05 percent SO_3. At 90 percent efficiency, the scrubber could operate at 100 percent lime stoichiometry.
G. Sludge G was produced by a double alkali system on the General Motors pilot plant burning high-sulfur oil with 100 percent excess air. The sludge solids consisted essentially of calcium sulfate with a minor amount of calcium carbonate and free carbon.

TABLE 46. IDENTIFICATION OF AICS SLUDGE STANDARDS (50)

STD I - Fly ash from Connecticut Light and Power Company's Devon Station.

STD II - CE sludge - $CaCO_3$, 150-percent stoichiometry, 2000-ppm SO_2.

STD III - Kansas Power and Light sludge.

STD IV - CE sludge - $Ca(OH)_2$, 38- to 50-percent stoichiometry, 50- to 60-percent SO_2 removal, slurry feed 220 gpm, recycle 165 gpm with 55-gpm blowdown.

STD V - Union Electric sludge.

STD VI - CE sludge - $CaCO_3$, 150-percent stoichiometry, 45- to 55-percent removal, no recycle.

STD VI A - STD VI plus 50-percent STD I (fly ash).

STD VII - CE sludge - 300- to 325-percent stoichiometry, 64-percent SO_2 removal, 300 lb/hr fly ash, 550 lb/hr $CaCO_3$.

STD VIII - CE sludge - 120- to 130-percent stoichiometry $Ca(OH)_2$, no fly ash addition.

STD IX - CE sludge - 220-gpm H_2O spray, 275 lb/hr lime feed, 300°F reaction temperature.

TABLE 47. WET CHEMICAL ANALYSIS OF SLUDGE STANDARDS (47)

(percent)

	STD I	STD II	STD III	STD IV	STD V	STD VI	STD VIA	STD VII	STD VIII	STD IX
SiO_2	46.7	1.5	30.7	0.79	19.4	1.1	27.7	4.6	1.2	2.0
Al_2O_3	23.2	0.32	6.6	0.05	6.8	0.01	14.7	2.3	0.48	0.45
Fe_2O_3	13.7	0.27	8.6	0.18	5.4	0.09	8.3	1.6	0.72	0.72
CaO	4.7	49.6	22.7	42.5	27.6	52.5	24.2	40.1	42.5	46.2
MgO	0.9	0.54	1.5	0.10	3.2	0.52	0.70	0.20	0.90	0.40
Na_2O	0.3	0.04	0.50	0.03	0.08	0.02	0.16	0.05	0.05	0.04
K_2O	2.6	0.17	1.1	0.05	0.24	0.14	1.2	0.29	0.07	0.21
TiO_2	1.5	<0.02	0.26	<0.02	0.32	<0.02	0.79	0.11	<0.02	0.02
P_2O_5	0.3	0.05	0.11	0.06	0.08	0.13	0.19	0.08	0.06	0.07
CO_2	2.6	29.2	5.3	3.7	7.2	36.6	15.3	13.6	11.5	24.4
SO_2	--	11.7	5.8	38.8	2.2	6.3	3.4	5.4	24.1	13.7
SO_3	0.8	3.5	6.5	3.3	12.3	0.5	<0.1	24.9	8.4	4.4
$CaCO_3$	5.9	65.7	12.0	8.4	16.3	80.6	34.7	30.9	26.1	55.4

Table 48 presents the results of chemical analyses for these sludges. X-ray diffraction studies on vacuum-dried sludge samples revealed that calcium sulfite hemihydrate was in the tailend lime scrubbing process. This compound was the main constituent of the sludge material other than flyash. A sulfate containing phase, ettringite, $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot XH_2O$, was found in the sludges containing flyash. Sludges produced by the limestone injection wet scrubbing process contained gypsum as a major phase (excess of 5 percent).[50]

TABLE 48. CHEMICAL ANALYSIS OF LIME PROCESS SLUDGES IN PERCENT ON DRY SOLID BASIS (50)

	A	B	C	D	E	F	G
CaO	18.1	43.2	40.7	43.4	25.6	43.8	25.6
MgO	2.4	0.2	-	0.01	1.2	-	1.2
Total S	7.2	18.9	18.1	20.0	10.9	22.9	8.4
SO_2	12.1	33.0	32.9	29.2	10.8	45.8	11.6
SO_3	2.9	5.9	4.8	13.6	13.6	0	6.4
CO_2	3.2	6.7	2.3	7.1	2.2	1.0	30.0
Free C	-	-	-	2.8	0.14	0	1.8
SiO	31.6	4.9	3.76	0.58	21.3	0.18	1.4
Al_2O_3	18.3	3.4	1.71	1.21	11.3	0.39	0.59
Fe_2O_3	4.3	0.6	0.86	0.39	5.6	0.29	0.27
Na_2O	-	-	-	0.35	0.76	0.09	0.52
K_2O	-	-	-	0.03	0.98	0.01	0.14
Free Base (as CaO)	0.3	1.3	7.9	0.06	0.06	0	0

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